# THE PHOTOLYSIS OF CERTAIN KETONES

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ABSTRACT

The work described in this dissertation was concerned with the photolysis of 2-pentanone, 4-methyl-2-pentanone and 2-hexanone in solution. The principal aim was to study the effect of variation of the solvent on the relative yields of the Type II elimination and the cyclization reactions. Both polarity and viscosity effects of the solvent were studied. The polarity effects were in accord with expectations based on current literature hypotheses which in turn are based primarily on work with aryl alkyl ketones. Small effects attributed to a solvent viscosity influence were observed for the first time and a tentative explanation for these is advanced. A novel reaction - photoketalization - which appears to occur without acid or base catalysis, was discovered. Possible mechanisms of the photoketalization are discussed.

As a basis for the interpretation of the results of this work, a critical review of the present state of knowledge about the photolysis of ketones is presented in the Introduction.

ACKNOWLEDGMENTS

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CONTENTS

# INTRODUCTION

A General Outline

The photochemistry of ketones has been, and doubtless will continue to be, the subject for a vast amount of research work. In the work to date two points are of particular interest in relation to the present investigation. One is the nature of the two lowest energy excited states open to an excited ketone and any possible differences between them. The other concerns the possible intermediates o[illegible]ng in the most common pathways of reaction of the excited ketone. It is the purpose of this introductory chapter to review these matters which are fundamental to an understanding of the present results. The arrangement of this review is described below.

Irradiation of a ketone with ultraviolet light leads to three main unimolecular reaction paths - Norrish Type I and Type II reactions, and cyclization. The latter two reactions will attract most attention in this dissertation, but all three are initially outlined in section B. The excited ketone formed by absorption of a photon is generally accepted to be either a singlet state or (following internal conversion), a triplet state. These two excited states of ketones are suggested to have different structures relative to the ground state and to exhibit differences in their reactivities, lifetimes and other properties (see section C). The principal method of determining the contribution of each state to the total nett photochemical reaction,

viz. quenching experiments, is also an important indicator of any differences between the states. Quenching experiments have been greatly refined in recent times and some of the earlier confusion and contradictory results, resolved. Some of the principal conclusions from such experiments with dialkyl ketones (the concern of this dissertation) are discussed in section C 3 of this chapter.

Norrish Type II elimination and cyclization are thought to occur via a common intermediate, which is now widely accepted to be a 1,4-biradical. It is clear, therefore, that an understanding of these photochemical reactions revolves around a knowledge of the factors affecting the formation and decay of this biradical. Some of the knowledge available at present is discussed in section D of this chapter.

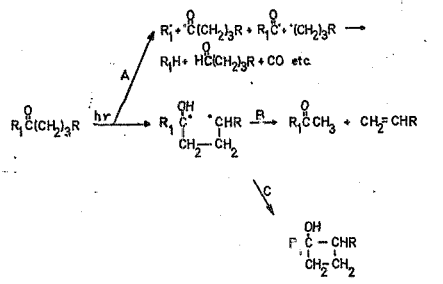
Most of the earlier photochemical studies of ketones were of the gas phase processes, but the greater amount of work today concerns the liquid phase. Many media effects on ketone photochemistry have been recorded in a rather fragmentary way in the literature. These are of particular importance in regard to the present work which is partly concerned with viscosity effects. To provide a basis for an understanding of the present results, the existing information is reviewed in section E.

In addition to the unimolecular photoreactions referred to above, a considerable number of bimolecular photoreactions of ketones have been described. It would be out of place here to refer to them all, since they are not directly relevant to the present work. However, hydrogen transfer from solvent is one such reaction that is relevant, and some aspects of this are therefore reviewed in section E.

B Basic Unimolecular Photoreactions of Ketones

Ketones exhibit three photochemical reactions that appear to be unimolecular in nature. One that is universally exhibited to varying degrees is the Norrish Type I reaction (Scheme I, reaction A), or α-cleavage into radicals [1,2]. The other two reactions take place only if there is a γ-hydrogen present in one of the alkyl groups. These two reactions are the Norrish Type II reaction leading to the elimination of an alkene [1] (Scheme I, reaction B), and a variant of the Type II reaction found by Yang, leading to a cyclobutanol [3] (Scheme I, reaction C).*

Scheme I

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* These reactions can usually be brought about with radiation of wavelength about 300nm. If, however, a shorter wavelength is used a Norrish Type III reaction (yield of $R_2C{=}CHCH_2R$) may occur [2]. This mode of reaction is negligible at 313nm [2,4].

The intramolecular hydrogen abstraction was first proposed by Noyes [5]. The ketone formed from reaction B (Scheme I) is initially produced in the enol form $R_1C(OH)=CH_2$ as was first shown experimentally by long-path infrared studies of the photolysis of gaseous 2-pentanone [6].

With ketones having alkyl sidechains of less than three carbons in length, Type I reaction is the major process. The probability of a Type I reaction, however, is reduced when a γ-hydrogen is present [7,8]. There is a further smaller decrease in Type I quantum yields when the type of γ-hydrogen changes from primary to secondary to tertiary [9,10]. Keeping such variables constant, the Type I reaction quantum yield appears to decrease with increasing alkyl chain length [11].

The fact that radicals are formed in the Type I reaction (Scheme 1, reaction A) was first proposed by Bamford and Norrish in 1935 [12] and has since been overwhelmingly proved. One would expect that the more stable the radical R·, the more likely it is to be a Type I fission product. Indeed, Yang has shown that 2-methyl-2-propyl ketones ($(CH_3)_3C$ COR [8], $((CH_3)_3C)_2$ [13]), undergo a considerable amount of Type I reaction in the liquid phase to produce the comparatively stable 2-methyl-2-propyl radical. Also Ausloos and Rebbert find that 90% of the Type I breakdown of 2-pentanone in the liquid phase produces $CH_3CO\cdot$ and $\cdot CH_2CH_2CH_3$ [14]. Furthermore, Pitts and Blacet, using light of wavelength 313nm to irradiate gaseous methyl ethyl ketone, found the amount of ethyl radicals produced was far larger than that of methyl radicals (40:1 at 100°C) [15].

However, some opposing findings have been reported. Guillet and coworkers have shown that in the liquid phase photolysis of 4-methyl-3-hexanone, products derived from the ethyl radical are formed

about 10 times more abundantly than those from the butyl radical [16] *. Also Nicol and Calvert, from a study of the gas phase photolysis of ketones of the type 1-PrCOR, have shown that the larger R group does not necessarily produce more Type I reaction [7]. It should be noted, however, that this latter observation is made on the basis of comparisons between the total Type I quantum yields of different ketones, and these yields will be influenced by the relative competitiveness of other processes. This competitiveness will in turn be influenced by variance in the nature of the group R.

In certain cases the Type I reaction is eliminated. Guillet and coworkers showed that with an α-methoxy group in the sidechain (2-methoxy-3-pentanone), no Type I products are formed [16]. (For a discussion of the effect of β-alkoxy groups see Introduction, section D1(b).) The Type II quantum yield for this compound is increased over that obtained from a similar alkyl ketone (4-methyl-3-hexanone) and a lower energy for the Type II transition state for the former is therefore proposed (rather than there being any inhibition of the Type I reaction).

All the types of photochemical reactions of ketones have been studied in both the vapour and liquid phases (except the Norrish Type III reaction which has only been observed in the gas phase). Type I quantum yields are much lower in the liquid phase than in the gas phase, probably at least partly because of a cage effect. In contrast it has been shown that the Type II reaction occurs roughly

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* They attribute this to a possibly greater efficiency of escape of the ethyl radical from the solvent cage as compared to the larger 2-butyl radical (see Introduction, section E3(a)).

in the same quantum yields in both phases [14,17]. However, the cyclobutanol seems to be formed to a greater extent in the liquid phase than in the gaseous phase irradiations. Indeed, only one or two authors have reported cyclobutanols in gas phase studies [6,14] - though this may be partly due to the fact that they often did not look for such compounds.

In 1967 Ausloos and Rebbert found a pressure effect on the photochemistry of gaseous 2-pentanone [14]. These authors found that, using 313nm irradiation, the quantum yield of the cyclobutanol (1-methylcyclobutanol) increased as the pressure increased (at 28°C and pressures between 0,13 and 32mm, photolyses produced quantum yields of 0,028 up to 0,108). A temperature decrease had the same effect (at a pressure of 15mm photolyses at 150°C and 28°C produced quantum yields of 0,044 and 0,075 respectively). Also the ratios of cyclobutanol : acetone (i.e. cyclization : elimination) under a variety of conditions of temperature and pressure, lay in the range 0,1 to 0,3 for the gas phase irradiation, while at various temperatures in the liquid phase the ratio lay between 0,4 and 0,5. It is reasonable to argue that if the reaction process is similar in the two phases (there appears to be no evidence to suggest otherwise), an effect similar to the gas phase pressure effect may be obtained in the liquid phase by varying the viscosity of the liquid. Indeed one of the aims of the work reported in this dissertation was to investigate this possibility using three similar 2-alkanones.

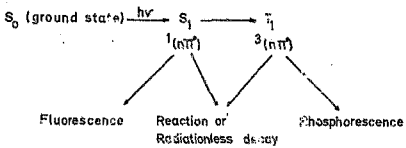
C Nature and Properties of the Ketone Excited States

1. Nature of the Ketone Excited States

The photon of excitation energy absorbed by the carbonyl group, usually leads to two electrons becoming orbitally decoupled. The electron spins, however, usually remain antiparallel and there is formed an electronic isomer of the ground state, called the excited

singlet state. The electron spins can become parallel forming the triplet state, the changeover being known as intersystem crossing (ISC). Both states may undergo radiative or non-radiative reversion to the ground state or chemical reaction. Numerous authors have observed that the natural lifetime of the singlet is less than that of the triplet state as its multiplicity is the same as that of the ground state. The diagram below (Scheme II) summarises these relationships:

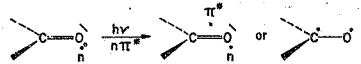
Scheme II




Any higher energy excited singlet state ($S_2$, etc.), rapidly cascades down to $S_1$ especially in the liquid phase [18]. Also almost all of the $T_1$ comes from intersystem crossing (ISC) and not direct absorption.

As regards ketones of the type relevant to the present work (e.g. 2-pentanone) both fluorescence and phosphorescence have low quantum yields in the gas phase and in solution [19,20]. Furthermore, the quantum yield of fluorescence and the singlet lifetime decrease as the chain length of the alkyl group increases [21]. Thus chemical reaction or radiationless decay would seem to be the principal fates of the electronically-excited states of simple ketones in solution.

Looking at the excited states from an "orbital" viewpoint, the singlet and triplet states have the configuration of $(n_o)^1(\pi^*)^1$ (commonly abbreviated to $n\pi^*$). The n orbital is more or less localised on the carbonyl oxygen atom while the $\pi^*$ orbital is delocalized over both the C and O atoms [18,22]. The $\pi^* \rightarrow n$ excitation may be represented as:




This model suggests that both states will exhibit electrophilic and radical-like character in the vicinity of the singly occupied n orbital on the oxygen and nucleophilic (and possibly radical-like) character above and below the carbonyl faces because of the presence of a $\pi^*$ electron [22].


2. Structure of the Ketone Excited States

Radiative transitions between states are governed by the Franck-Condon principle which requires all transitions to be vertical, i.e. involve no change in internuclear distances. The rationale is that electron movements are faster than nuclear movements. A variety of vibrational states are available to any electronic state and therefore both the absorption and emission spectra will consist of closely spaced lines corresponding to different vibrational energy changes. The most probable transitions occur from the ground vibrational state

when the internuclear distance is the equilibrium value. In the case of higher vibrational states, however, the most probable transitions occur when the molecule is near one of the turning points of the vibration. The implication of the Franck-Condon principle is that the excited state reached by absorption of radiation, must have the same geometry as the ground state. However, this geometry need not be the preferred equilibrium geometry of the excited state.

As seen before the electronically-excited carbonyl group is virtually a singly bonded entity and it would not be at all surprising if its equilibrium geometry differed from that of the ground state. The fact that there is a large difference between the energies of absorption and emission of acetone indeed implies such a geometric change between the ground and excited states [23]. The explanation advanced is that the Franck-Condon excited state molecule (planar about the carbonyl group) has a long enough lifetime to relax to pyramidal geometry before emission. Indeed, direct spectroscopic investigation has shown that equilibrium triplet formaldehyde is out of plane (pyramidal) by 35° while the singlet state is out of plane by 20° [22,24]. Wagner, on the basis of the results of experiments with acetone, has also suggested that the triplet state is more puckered than the singlet state in the case of alkanones [25]. As regards other alkanones O'Sullivan and Testa, from a study of a number of examples, suggest that an increase in the alkyl group size decreases the energy difference between the planar Franck-Condon excited state and the pyramidal equilibrium excited state from which emission (and probably reaction) occurs [26].

The overall conclusion is that the Franck-Condon principle is not a reliable guide to the geometry of the excited states of ketones.

The non-occurrence of Franck-Condon geometry may complicate steric interpretations of excited state properties.

3. Differences in Photoreactivity Between Singlet and Triplet States

(a) Methods of study

Because of their distinctive properties the singlet and triplet excited states can be expected to make different contributions to the nett photochemical change. These different contributions may be revealed by comparing the photoreactions in the presence or absence of added quencher. A quencher is a substance which can accept the singlet or triplet excitation energy of the ketone, the theoretical requirement for this being that its energy of excitation is lower than that of the ketone in question *. It is believed, for example, that 2,3-butandione is able to quench the singlet state of simple ketones [28] (and hence also prevents formation of triplets), whereas dienes (such as 1,3-pentadiene) quench only the triplet state of most ketones [29]. The mechanism is usually thought to be a physical energy transfer process concerning which there are many theories [30], but it has also been suggested that the quenching may be of a chemical nature in some cases [31]. In the energy transfer process, the acceptor or quencher usually takes on the same spin state as the excited donor [32]. The most important fact in relation to quenching in solution, is that the rate of the process is usually diffusion-controlled (except in media of low viscosity [33]) due to donor and acceptor having to move through the solution in order to encounter one another when facile energy

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* Although experimental results are generally consistent with this expectation, Yang has reported cases of inconsistency [27].

transfer may occur *. Recent experiments suggest that van der Waals contact distances are sufficient to permit energy transfer [34]. Hence steric hindrance to energy transfer seems to be rarely found.

The effectiveness of a quenching process can be measured by using the Stern-Volmer plot. It can be shown that [32]:

$$\frac{\phi_o}{\phi_A} = 1 + k_q \tau [A]$$

where $[A]$ is the concentration of the quencher (A); $\phi_A$ and $\phi_o$ are the quantum yields of reaction (or other processes) with and without A respectively; $k_q$ is the rate constant for quenching (approximately equal to the rate of diffusion); $\tau$ is the lifetime of the state being quenched.

From this then it can be seen that a plot of $\frac{\phi_o}{\phi_A}$ $[A]$ should give a straight line with an intercept of 1 and a slope equal to $k_q \tau$.

Whatever the nature of the energy transfer process, it appears generally to occur at a rate close to the rate of diffusion - and this assumption is often made. There are a number of observations however which suggest that this assumption should be made with caution. For example, Wagner has found that the rate of triplet quenching and the rate of diffusion are roughly the same in 2-methyl-2-propanol and that they are both proportional to the reciprocal of viscosity [35]. However, on using a hydrocarbon of the same viscosity the rate of quenching was about half that found in 2-methyl-2-propanol.

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* There are other quenching mechanisms (e.g. long range transfers) but these are less common and are unlikely to be important in the kinds of experiment reported here.

Again, in more recent work, Wagner has shown that if a solvent has a viscosity less than about three centipoise, the rate of energy transfer may be less than that of diffusion, i.e. the energy transfer is then not totally diffusion-controlled [33]. For solvents with viscosity higher than three cP, the rate of energy transfer (quenching) approximately equals the rate of diffusion. However, many authors still equate the rates of quenching and diffusion for all solvents. Thus any kinetic work reported in the literature which has been done using solvents of low viscosity and in which this assumption has been made, must be considered possibly unreliable.

Another point of caution has been raised by Turro and coworkers [36]. They have shown that 1,3-pentadiene quenches some of the singlet as well as the triplet states of ketones. This partial quenching (of the fluorescence) of the singlet state is only important for high concentrations of the diene (> 1M).* In these circumstances a modified Stern-Volmer expression must be employed [38]. In view of these findings it is evident that the practice of attributing the reduction in overall quantum yield at high quencher concentrations to elimination of the triplet contribution to the reaction, is an unwise one.

Additional information about the characteristics of the different excited states and their involvement in ketone photochemistry, has also been gained by less obvious methods. An example is the use of aryl alkyl ketones to demonstrate effects most probably present in alkanones. This is due mainly to the large proportion (sometimes

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exclusive) of triplet state reaction in aryl alkyl ketones [10,39,40,41] which permits a comparatively easy study of triplet state properties and how they are influenced by structure, solvent, etc. The applicability of this approach depends on establishing that it is the $n\pi^*$ state which is the reactive state of the aryl alkyl ketone and not the $\pi\pi^*$ state [41,42,43,44].

(b) Results and conclusions

Study of the participation of the singlet and triplet states of ketones in ketone photoreactions has been extensive, and only the main results will be outlined in the following pages. Since the Type II reaction and cyclobutanol formation are the principal points of interest in this dissertation, most of the discussion centres around these two reactions. It may simply be noted here that it appears that *the Type I reactions in solution may take place from either state* exclusively [45,46] or partly from both [8,13].

The presently accepted position is that the cyclization and the elimination reactions occur from both the singlet and triplet state. This was first shown by Wagner and Hammond who found that 1,3-pentadiene did not stop all the elimination and cyclobutanol formation from 2-pentanone in the liquid phase [10]. At about the same time Dougherty came to the same conclusion regarding the photolysis of liquid 2-octanone [47] from the levelling off of a Stern-Volmer plot for higher quencher concentrations.

A number of authors have investigated the contribution of singlet and triplet states to the total observed elimination and cyclization [10,28,48,49]. It appears that most of the cyclization comes from the triplet state. Elimination (Type II reaction) is the major reaction of the singlet state but nevertheless elimination products may be obtained from the triplet state in substantial yields -

sometimes larger than the yields from the singlet state. The case of 5-methyl-2-hexanone is probably typical. In hexane Yang and Elliott found that the total quantum yield (elimination and cyclization) was 0,077 from the singlet and 0,076 from the triplet [48]. However, the partitioning between elimination and cyclization was 12:1 for the singlet state and 3:1 for the triplet state.

The possibility of a connection between the length of the alkanone sidechain and changes in quantum yield of the elimination and cyclization reactions, or amounts of participation by either excited state, has received some attention in the literature. Pitts and coworkers studied phenyl alkyl ketones with alkyl sidechains varying from three to ten carbon atoms in length [50]. They found no change in either the quantum yields of the elimination and cyclization reactions or the lifetime of the triplet state. Wagner and Kemppainen later confirmed this [51].

Guillet and coworkers have studied this point using alkanones [11,52]. They found, in contrast to the above-mentioned results, that the quantum yield of the elimination reaction dropped as the chain length increased [11]. However, while the elimination reaction yields from both the singlet and triplet states decreased, the ratio of singlet to triplet elimination yields remained constant. The quantum yield of cyclobutanol formation also appeared to diminish with increasing chain length [52]. They reasoned that increasing radiationless decay occurred with increasing chain length (see introduction, section D 2 (e)).

As noted earlier there is considerable evidence that both singlet and triplet ketone states undergo elimination and cyclization via the 1,4-biradical formed by intramolecular hydrogen abstraction. In addition, radiationless decay of the states probably involves the same

intermediates (see introduction, section D2 (e)). It follows that factors which influence the rate of γ-hydrogen abstraction by the first-formed singlet should affect the proportion of nett reaction occurring via the singlet state. Amongst structural factors which influence the proportion of singlet and triplet reactions in this way are the nature and number of γ-hydrogen atoms, the substitution of deuterium for γ-hydrogen and the length of the alkyl chain. These will be discussed in the following sections which are concerned with the properties of 1,4-biradicals.

D 1,4-Biradical Intermediates In Photoreactions of Ketones

As mentioned earlier, irradiation of ketones having a γ-hydrogen, leads to Type II reaction and cyclobutanol formation. Initially there was much debate as to whether either reaction (Type II reaction or cyclobutanol formation) was concerted or involved a 1,4-biradical. Bamford and Norrish first formulated the mechanism of their Type II reaction without radicals [1] and a concerted mechanism was postulated by many authors including Ausloos and Rebbert [14]. However, these authors found that pressure and temperature affected only the cyclization and not the elimination reaction [14]. This would perhaps suggest that only the latter may be concerted. Another interpretation of this result is that the difference may be no more than a difference in the vibrational (or other) energy content of the intermediate species.

The balance of opinion at the present time is probably that both nett reactions proceed through a common intermediate, which is proposed to be a 1,4-biradical, formed by the intramolecular abstraction of the γ-hydrogen by the excited carbonyl. The evidence concerning this will be referred to in the sections below, but for convenience of

discussion of mar. aspects of ketone photochemistry relevant to the present studies it will be accepted as a working hypothesis.

In the sections that follow, therefore, factors relating to formation of these biradicals and to their properties will be reviewed.

1. Formation of 1,4-Biradicals

(a) Radical nature of the excited carbonyl group

The excited carbonyl may be compared to an alkoxy radical:


In terms of a simple valence bond picture they are similar [53] and indeed they show similar selectivity towards hydrogen abstraction from carbon-hydrogen bonds [41,54,55]. For example, triplet benzophenone in intermolecular hydrogen abstraction reactions, displays a selectivity towards C-H bonds of different strengths, similar to that shown by 2-methyl-2-propoxy radicals [54]. A similar correlation is found for the intramolecular hydrogen abstraction rate constants of the triplet benzoyl group [41,55]. Whatever the best representation of the excited carbonyl actually is, the fact that the radical-like oxygen abstracts hydrogen atoms, is firmly established.

(b) Nature of the abstracted hydrogen atom

Srinivasan first showed that the γ-hydrogen was abstracted [56]. He studied the gas phase photochemistry of 5,5-dideutero-2-hexanone and obtained deuterated acetone. He also obtained some ordinary acetone and proposed either β-hydrogen abstraction or hydrogen exchange

on the walls of the reaction vessel to account for this. Using $D_2O$ and 2-hexanone, he then proved exchange can take place and decided that it must be the γ-hydrogen that is abstracted*. This was further supported by Coulson and Yang who ared the photochemistry of 2-hexanone,5-deutero-2-hexanone and ; ;-dideutero-2-hexanone [17]. They found deuterated propene and cyclobutanol in addition to deuterated acetone from the deuterohexanones. They also found that the quantum yield of the reactions was dependent on the γ-substitution, decreasing from 5,5-dideutero-2-hexanone to 2-hexanone. They suggested that the deuteration increases the amount of triplet state formation, thus increasing the quantum yield of reaction as the triplet gives a greater proportion of products relative to decay, than the singlet. Borkowski and Ausloos also found this kind of difference resulting from the presence of either hydrogen or deuterium in the γ-position [58]. In addition they found that the ratio of the yields of products formed by hydrogen and deuterium abstraction, decreased with increasing temperature. Since the strength of the C-H bond is less than that of the C-D bond, this suggests that as temperature increases so the C-X bond strength becomes a less important factor. However, since temperature affects so many other factors (e.g. singlet and triplet state reaction rates or quantum yields, etc.), this interpretation may not be reliable. The γ-deuterium isotope effect mentioned by many authors [17,59,60,61,62] must certainly indicate the involvement of γ-hydrogens however.

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* A similar procedure (deuteration of the γ-position) also showed that it is from this position that intramolecular abstraction occurs, in the McLafferty mass spectroscopic breakdown of ketones with γ-hydrogens [57].

Many studies have been made of the relation between C-H bond strength, the rate of intramolecular hydrogen abstraction and the quantum yields of reaction from singlet and triplet states. The C-H bond dissociation energies decrease as the nature of the γ-hydrogen varies from primary to secondary to tertiary. (Benson quotes dissociation energies (D) for the different principal types of C-H bonds as follows: primary D = 410kJ $mol^{-1}$, secondary D = 395kJ $mol^{-1}$, tertiary D = 381kJ $mol^{-1}$ [63].) Many groups, e.g. Barltrop [64], Hammond [10], Ausloos [65] and Yang [28,66] and their coworkers have shown that there is an increase in the rate of abstraction as the type of γ-hydrogen is varied by increasing the γ-substitution with alkyl groups. The same selectivity towards γ-hydrogens has been found in studies using aryl alkyl ketones [40,50] and diketones [67] and also in the mass spectroscopy of ketones [57] (McLafferty breakdown).

Internal competition using a ketone with different types of γ-hydrogens on the two sides of the carbonyl has been studied. In a liquid phase study Wagner used 4-octanone which has a primary γ-hydrogen (Type II reaction leads to 2-hexanone and ethene) and a secondary γ-hydrogen [49] (Type II reaction leads to 2-pentanone and propene). On isolating the ketonic products from the photolysis, with and without quencher, he found the secondary to primary abstraction ratio was 12:1 for the singlet and 17:1 for the triplet state. (This lower selectivity of the singlet state has also been shown in a similar way by Padwa and Bergmark in regard to selectivity for γ-hydrogen versus γ-deuterium [59].)

Ausloos used 4-methyl-2-hexanone in ethanol in a study of temperature effects on selectivity [68]. He compared the olefinic products (from Type II reaction) and found that the ratio of 2-butene (secondary γ-hydrogen abstraction) to 1-butene (primary γ-hydrogen

abstraction) was 16,2 at 28°C and that this value decreased as the temperature increased*. As with the deuterium studies, the observed effect suggests that the strength of the γC-H bond becomes of less importance as the temperature increases. As was mentioned before, with temperature affecting so many other variables, this interpretation is not necessarily correct.

One of the most comprehensive quantitative studies showing the consequences of variation in the degree of substitution of the γ-carbon, is that of Yang and coworkers [28]. They studied 2-pentanone, 2-hexanone and 5-methyl-2-hexanone in hexane. They found that as the γC-H bond gets weaker, the quantum yield of singlet reaction (and singlet radiationless decay) increases. At the same time the quantum yields of intersystem crossing and triplet reaction decrease - although the rate of intersystem crossing does not vary much. However, the relative decrease in quantum yield for intersystem crossing (reflecting the amount of triplet state formed) is greater than the corresponding relative decrease in quantum yield for triplet reaction - suggesting that the reactivity of the triplet also increases as the γC-H bond strength decreases. (Such an effect on triplet state reactivity has also been demonstrated for aryl alkyl ketone [40]).

As the type of γ-hydrogen influences the quantum yield of reaction, so does the number of γ-hydrogens. Pitts showed this by comparing the results of irradiation of (i) 4-methyl-2-pentanone and (ii) 4,4-dimethyl-2-pentanone [69]. He found that (ii) had a greater

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* Below -100°C the trend was reversed. In the gas phase both the temperature and the wavelength affected the ratio, but in solution while the temperature effect remained, the wavelength used had no significant effect. In solution, the solvent had no effect either.

quantum yield of reaction than (i) and that the ratio of the quantum yield of the Type I reaction (determined by the amount of carbon monoxide) to the quantum yield of Type II reaction products was larger for (i) than (ii). Both results were attributed to the number of γ-hydrogens being greater in (ii) than (i). This effect of number of γ-hydrogens was further shown by Nicol and Calvert who studied the gas phase photochemistry of 1-propyl alkyl ketones, 1-PrCOR, having γ-hydrogens on either side of the carbonyl [7]. Within one ketone there is a good correlation between the number of γ-hydrogens and the quantum yield of Type II reaction for each sidechain. In the case of 2-butyl 1-propyl ketone ($CH_3CH_2CH_2COCH(CH_3)CH_2CH_3$ - one set (of three) primary γ-hydrogen on R), the quantum yields of Type II reaction for each sidechain are approximately equal, while for the 2-methyl-1-propyl 1-propyl ketone ($CH_3CH_2CH_2COCH_2CH(CH_3)CH_3$ - two sets (of three) primary γ-hydrogens on R) the ratio is 2,7:1. However, when comparing the total Type II quantum yields there is no simple correlation between them and the total number of γ-hydrogens present in the compound. For example although di(1-propyl) ketone and 2-methyl-1-propyl 1-propyl ketone contain two and three sets (of three) γ-hydrogens respectively and methyl and ethyl 1-propyl ketones each contain one set (of three), the Type II quantum yields are about the same for all four ketones [7].

It seems therefore that where internal comparisons can be made the effect of number and type of γ-hydrogen has been demonstrated. However, comparisons of quantum yields from different ketones are complicated by the effects of structure on other excited state processes, e.g. radiationless and radiative (in the gas phase) decay, and it is not possible to use such comparisons for the same purpose.

It has been found that the presence of an oxygen atom in the sidechain (as in α-alkoxyketones) results in an increase in the quantum

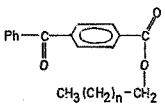
yield of Type II reaction [16,70]. This may be due either to a reduced bond dissociation energy of the γC-H bond (the γ-hydrogen abstraction rate constant for methoxyacetophenone is 230 times that for butyrophenone [40]) or to easier formation of the six-membered transition state or both. A corresponding increase in the quantum yield of oxetanol formation has been observed in the case of aryl alkyl ketones [42] (dialkyl ketones with α-alkoxy groups do not form oxetanols [16,71]).

An increase in the rate of γ-hydrogen abstraction can also be seen for γ-methoxy ketones [40]. Other substituents of similar character (e.g. $OH$, $NH_2$) on the γ-carbon increase the reactivity towards γ-hydrogen abstraction while groups of opposite character (e.g. Cl, COOMe, CN) have the inverse effect [41,51]. Wagner and Kemppainen have shown that the inductive effects on γ-H reactivity noticed for substituents at the γ-position, also appear weaker with substituents in the δ, ε (smaller effect) and ω (smaller yet) positions [51].

With straight chain alkyl groups larger than $C_4$, the γ-hydrogen atoms are formally all the same and one would not expect any differences in the quantum yield for their abstraction. As mentioned earlier (see Introduction, section C 3(b)) both Pitts [50] and Wagner [40,51] have found this to be so in a series of aryl alkyl ketones. But Guillet and coworkers do find a regular decrease in the Type II quantum yield as the alkyl group size increases in a series of dialkyl ketones [9,11] (see also Introduction, sections D 2(c), (e)).

In some cases a hydrogen other than a γ-hydrogen can be abstracted. It usually seems to occur either when there is no γ-hydrogen available (e.g. unbranched β-alkoxy ketones : Ph $COCH_2CH_2OCH_3$) or another hydrogen is better positioned or more labile to attack due to some

structural peculiarity of the molecule. Turro has shown by deuterium labelling that an α-hydrogen is abstracted to form an enol [72] In the case of diketones [72,73]. A number of authors have used β-alkoxy ketones and found that some tetrahydrofurans (δ-hydrogen abstraction) are formed [74]. δ-Hydrogen abstraction in δ-methoxyvalerophenone has recently been shown by Wagner and coworkers [75]. There seems to be some dispute as to the general importance of δ-hydrogen abstraction but the possibility of its occurrence may be taken as proven. Abstraction at even more remote sites has been observed in the compounds shown below [76]:




n > 9

All the foregoing results emphasize the significance of steric accessibility of the hydrogen for intramolecular abstraction. It is consistent with this that when a γ-hydrogen is held in position to facilitate abstraction, photoreactivity may be increased. Padwa and coworkers have done much work in this field [77,78] and demonstrated the possibility of promoting cyclization or elimination in this way (see introduction, section D 2(c)). It appears, for example, that significant amounts of cyclization may occur from the singlet state when the stereochemical situation is particularly favourable [79].

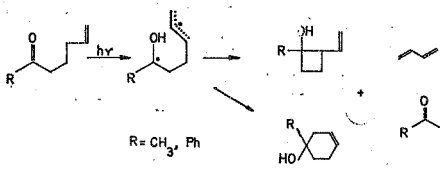
2. Properties of 1,4-Biradicals

The postulate of the intermediacy of 1,4-biradicals depends for its success on its ability to account in a unified way for a number of ketone photoreaction phenomena. Some of these phenomena are discussed below in a manner which emphasises the relationship of these phenomena to the presumed properties of the 1,4-biradical. In the historical development of the biradical postulate, these phenomena have been regarded as evidence for the validity of the postulate*.

(a) 1,4-Biradicals and double bond migrations

Yang and coworkers observed that 1-hepten-6-one on irradiation yielded both a cyclobutanol and a cyclohexenol in a 4:1 ratio [20] (Scheme III; R = $CH_3$). Padwa obtained analogous results with the related ary ketone (R = Ph) [77].

Scheme III




* The use of 1,4-biradicals in chemical explanations is fairly common. For example, a 1,4-biradical is the generally accepted intermediate in the photocycloaddition of ketones to olefins [22].

The simplest explanation of these observations is that a 1,4-biradical is formed by γ-hydrogen abstraction and that the radical centre at the γ-carbon is conjugated with the adjacent double bond. The resulting allylic radical can participate in cyclization at either terminus, the one mode corresponding to nett migration of the original double bond.

This reaction was substantially quenched by 1,3-pentadiene but not entirely [28], and Yang and coworkers therefore concluded that both singlet- and triplet-derived 1,4-biradicals participated.

Allylic delocalisation may of course occur in concert with the γ-hydrogen abstraction (i.e. occur "instantaneously") provided the conformation of the alkenyl chain is at least approximately correct. In such circumstances γ-hydrogen abstraction should be facilitated. Indeed this may be the reason for the high quantum yield of cyclobutanol found in the photoreactions of α-diketones [80] and αβ- [81] and βγ- [82] unsaturated ketones.

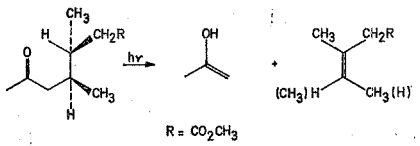
(b) 1,4-Biradicals and racemization at the γ-carbon and related phenomena

If a 1,4-biradical is formed from a ketone with an asymmetric carbon γ to the carbonyl group, a configurational change may occur at the γ site before reaction or radiationless decay (through back donation of the γ-hydrogen (see Introduction, section D 2(e))). Thus products or recovered ketone may be found which show configurational change at the γ site. The configurational change requires internal rotation about the β-γ bond, so whether or not configurational change is observed depends upon the rate of this rotation relative to reaction and radiationless decay. There has been considerable experimental and theoretical interest in these phenomena and the interpretations are as yet incomplete.

Yang has shown that in the photolysis of S-(+)-5-methyl-2-heptanone, the R-isomer of the starting ketone forms [48]. Quenching studies showed, however, that the R-isomer formed only from the triplet state. Consistent with this observation is the finding that S-(+)-4-methyl-1-phenyl-1-hexanone, a ketone which reacts predominantly from the triplet state, undergoes extensive photoracemization [60] *.

Stephenson obtained slightly different findings from a study of the Type II olefinic products of photolysis of erythro- and threo-3,4-dimethyl-6-ketoheptanoate (Scheme IV) [83].

Scheme IV




R = $CO_2CH_3$

The erythro ester gave a cis:trans ratio of 90:1 for the singlet-derived products (30% of reaction) and 1:1 for the triplet-derived products. Likewise the threo ester gave a cis:trans ratio of 1:90 for the singlet-derived products (15% of reaction) and 1:1,5 for the triplet-derived products. Gano made a more limited study of the photolysis of erythro- and threo-1,2-dimethylbutyl acetate and noted that no racemization of the recovered ester could be detected [84].

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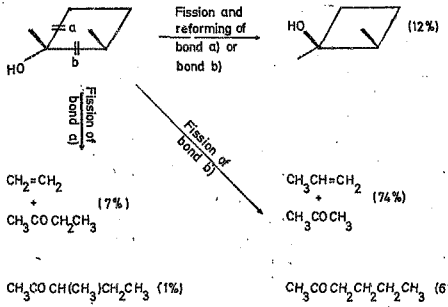
* It is interesting to note that this ketone has quantum yields of 0,26 for products and 0,78 for photoracemization in benzene while in a polar solvent (2-methyl-2-propanol) they are 1,00 and 0,00 respectively [41,60]. This suggests that reaction and racemization come from a common 1,4-biradical.

Very recently, Casey and Boggs have reported studies of the stereochemistry of the Type II olefinic products from a simple ketone [62]. Using erythro- and threo-5-deutero-4-methyl-2-hexanone, they found 90 to 95% stereoselectivity of olefin formation from the singlet state and a much lesser stereoselectivity from the triplet state.

The high stereoselectivity of singlet reactions is further evident when the photolysis of a cyclobutanone is considered. In contrast to other cycloalkanones, Turro found that photolysis of cis- and trans-2-ethyl-3-methoxycyclobutanones was unquenched by 1,3-dienes and was not accompanied by photoepimerization [85]. The implication is that stereospecific reaction from a singlet state occurs, although the possibility of an unusually reactive triplet state which evades quenching cannot be discounted.

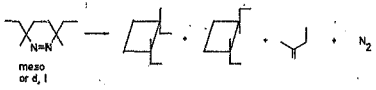
Stephenson has discussed the possible origin of the different behaviour of the singlet- and triplet-derived biradicals in a number of published works [83,86]. Initially, to explain the high stereoselectivity associated with the singlet state, he considered the possibility that reaction might occur via a reversal of the "ene" reaction [83] (which is completely stereospecific [87]). However, on the basis of an argument involving steric effects, this possibility was discounted in favour of a singlet biradical intermediate. Stephenson also drew attention to the interesting comparisons that may be made with the results of the pyrolysis of cyclobutane derivatives. Pyrolysis takes place only from the singlet state of course, and 1,4-biradicals have frequently been postulated as intermediates. For example, Feit has described the pyrolysis of cis-1,2-dimethylcyclobutanol (Scheme V) at 381°C in which he found that the thermal decomposition gave products similar to those from the photochemical reaction of 2-hexanone [88].

Scheme V




The cis-trans isomerization strongly suggests a biradical intermediate. This is supported by the results of Bartlett and Porter's study of the azo compound shown in Scheme VI [89]. Thermal and direct photolytic decomposition (via singlet state) of one stereoisomer (d) or meso) of this azo compound gave products showing a few percent loss of configuration, but loss of configuration was more extensive (35-40%) in the photosensitised decomposition (via the triplet state).

Scheme VI




Pyrolyses of cyclobutanes on the other hand generally show a low stereoselectivity [90,91].

The general conclusion from all the studies described above is obviously that bond rotation is probably always competitive with reaction in triplet 1,4-biradicals and may also be in the case of singlet 1,4-biradicals. More detailed conclusions are arrived at with difficulty as Stephenson and his coworkers have clearly shown [86]. The basic difficulty perceived by Stephenson and Braumen was that a thermochemical analysis of the cyclobutane pyrolysis data implies that there appears to be an energy barrier of some 25 to 33kJ $mol^{-1}$ for closure or cleavage of singlet 1,4-biradicals [86a]. In turn this implies a rotational barrier in such biradicals of 42kJ $mol^{-1}$, at least in tertiary biradical systems. However, application of such a rotational barrier to the triplet biradical gives rise to the deduction of an unreasonably long triplet lifetime. Their initial response to this dilemma involved consideration of the PE diagram shown in Figure 1.

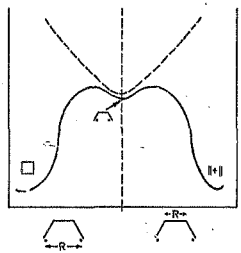



Figure 1 : Potential energy diagram for 1,4-biradicals

The solid curve is a reaction coordinate diagram appropriate to the thermally equilibrated singlet 1,4-biradical transforming either into cyclobutane or olefines. An energy barrier exists for either of these processes, rendering them slow relative to bond rotation. If vibrationally "hot" 1,4-biradicals are generated, however (as in Bartlett's [89], Stephenson's [83] and Yang's work [48]) they may have energies such that regions of energy space corresponding to energised products are readily accessible. Thermally equilibrated products may thus be formed stereoselectively if vibrational deactivation competes effectively with bond rotation, which was considered likely.

The dotted curve represents the corresponding triplet 1,4-biradical situation. It is strongly repulsive in both directions and, provided vibrational deactivation is fast relative to spin inversion, the triplet biradical will invariably relax into the energy minimum. A lack of stereoselectivity similar to that of vibrationally equilibrated singlet 1,4-biradicals is thus expected.

An alternative resolution of the dilemma is offered by Stephenson and Gibson in a later paper [86b]. In the previous argument, there is an implicit assumption that the bond rotation barriers of the singlet and triplet biradicals are equal or similar. However, from molecular orbital calculations they determine that the singlet biradical most likely has a greater barrier to bond rotation than the triplet biradical. The problem thus appears to be resolved since the initial assumption of Stephenson and Brauman (which led to this problem) may be false.

Casey and Boggs in a recent contribution on the same problem [62] tend to favour the earlier views of Bartlett and Porter, advanced in connection with their azo compound studies [89]. Bartlett and Porter proposed that the triplet biradical has a longer lifetime than the singlet biradical since it must undergo spin inversion back to

the singlet state, prior to formation of ground state products. Loss of stereochemistry is due to the greater chances of rotation in the longer lived triplet biradical.

This was discounted by Stephenson partly because he could not reconcile the notably differing stereoselectivities of the singlet 1,4-biradical, derived from different types of reactions [86a]. Casey and Boggs claim that this reconciliation is no problem because the *rates of rotation of singlet 1,4-biradicals vary with their structure* [62]. They quote an estimate of Bergman and Carter that the rate of rotation about a secondary radical centre is an order of magnitude greater than the rotation about a tertiary (more ponderous) radical centre [92]. Valid comparisons of singlet 1,4-biradicals can only be made therefore, when they have similar structures. A considerable body of information is then successfully correlated by recognising this.

*The conclusion as regards* singlet 1,4-biradical behaviour would appear to be uncertain at this stage though the simplicity of Casey and Boggs' explanation is appealing. Further critical experimental data will be needed to clarify the situation. However, it does appear generally valid to claim that greater stereoselectivity is exhibited in singlet 1,4-biradical reactions than in triplet 1,4-biradical reactions. This does not necessarily imply however, that high stereoselectivity implicates a singlet 1,4-biradical. Turro, for example, has reported that irradiation of the optically active diketone S-(+)-4-methyl-1-phenyl-1,2-heptandione resulted in no photoracemization in the recovered ketone* despite reaction occurring largely from the

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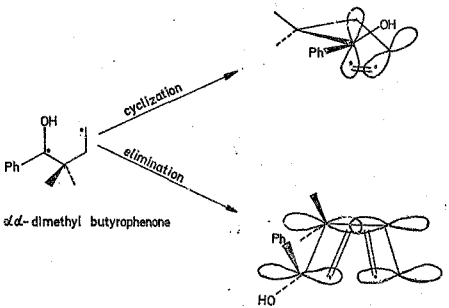
* The amount of retention of optical activity in the recovered cyclobutanone was not known [72]. However, in a later review, Wagner reported that this diketone produces a cyclobutanone mixture with a small optical rotation [41].

triplet state [72]. Possibly the additional hetero atom present in this system exerts a special effect, e.g. stereochemical control through bridging [93].

(c) Steric effects on reactions of 1,4-biradicals

1,4-Biradicals are embodied in an explanation of the effects of α-methyl substituents on alkanone photochemistry, observed by Nicol and Calvert [7]. The explanation, due to Lewis, followed his own work on aryl alkyl ketones [94]. He used PhCOR where R contained various numbers of α, β or γ methyl substituents. Intramolecular hydrogen abstraction leads to a 1,4-biradical which adopts different conformations for cyclization and for elimination. The transition state for cyclization requires the overlap of the radical centre orbitals (Scheme VII), and α-substituents cause this state to be more favourable since 1,2-eclipsing interactions are avoided in this mode of reaction. This explains the increase in the quantum yield of cyclobutanol and

Scheme VII

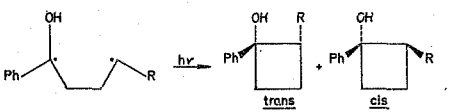



α,α-dimethyl butyrophenone

decrease in the quantum yield for Type II elimination caused by increasing the number of α-methyl groups from none to two (increase in the relative amounts of cyclobutanol formation from 10% to 29% to 89% respectively for a series of butyrophenones). Lewis has also argued that the most favoured transition state for elimination requires maximum overlap of both singly occupied orbitals with those of the bond undergoing cleavage. β-Methyl substituents, by avoiding 1,3-eclipsing interactions, should favour this, as indeed was found to be the case, although the effect was smaller than that caused by α-methyl substituents. There was a corresponding decrease (smaller effect than for the α-methyl substituents) in the quantum yield of cyclobutanol. Lewis also found the effect of γ-methyl substituents was negligible apart from the effect on the γ-hydrogens already discussed. If geometrically isomeric cyclobutanols could be formed, a marked preference for formation of the trans isomer was seen [94]

Wagner and coworkers have recently reported similar results from an extensive study of a number of phenyl ketones [95,96] (which are believed to react exclusively from the triplet state). They also note the preference for formation of trans-cyclobutanols and suggest that the comparative magnitude of developing non-bonding interactions in the transition state for cyclization may explain this. Somewhat unexpectedly they find that increasing γ-alkyl group size, increases the relative amount of cis-cyclobutanol so that the cis/trans ratio approaches unity. The authors think the only possible interpretation is that the rate of $C_\beta$-$C_\gamma$ bond rotation in the biradical is comparable to the rates of chemical reaction of the biradical. A similar interpretation is given to the observation that the cis/trans ratio inc[illegible] in going from benzene to 2-methyl-2-propanol to wet acetonitrile as solvent, solvation of the hydroxyl group of the biradical

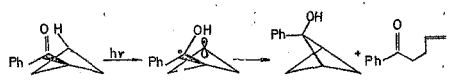
causing increased bulk of the latter (see Introduction, section E2).




These findings are compatible with Bergman's views about the relative rates of rotation in radicals of different structure which were mentioned in the Introduction, section D2(b) [92]. It is suggested that the 1,4-biradicals are formed initially (by γ-hydrogen abstraction), with equal probability in conformations appropriate to formation of cis- and trans-cyclobutanol. Then the slower rate of rotation of the more bulkily substituted (or solvated) biradical would indeed give rise to a lesser preponderance of trans- over cis-cyclobutanol product.

The difference between the preferred biradical conformations for elimination and cyclization also features in Wagner's [40,41] interpretation of some results of Padwa [97]. Padwa found that phenyl cyclobutyl ketone gave a lower quantum yield of photoproducts than valerophenone but that there was 60% cyclization to a highly strained bicyclopentane system and only 40% elimination to the strain free acyclic system (Scheme VIII). Thus product stabilities do not govern the preferred

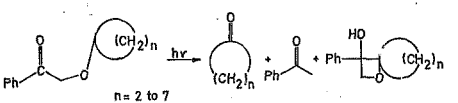
Scheme VIII



reaction but the relative energies required to reach the necessary transition state conformations may [41]. The predominant formation of a cyclobutanol from 1-adamantyl acetone was explained by Turro in an analogous fashion [98] *.

There are two other results that deserve mention since the explanation of them may well reside in a steric effect in the biradical. One is that irradiation of cis-2-(1-propyl)-4-(2-methyl-2-propyl)-cyclohexanone leads to Type II reaction whereas the trans isomer only forms the cis isomer [100] (presumably in a short-term irradiation!). A stereo-electronic effect appears to be operative as in the cis isomer it is easier to obtain a six-membered ring transition state since the γ-hydrogen may be held in the plane of the carbonyl group, and/or the β-bond is positioned for elimination. Others, using the same cyclohexanone, have shown this effect to be manifested by both singlet and triplet states [101]. The second result relates to the photochemistry of α-cycloalkoxyacetophenones (Scheme IX) [102]. The quantum yield of

Scheme IX




* However, Sauers and coworkers have suggested that in bicyclic ketones, the difficulty of introducing a double bond in a strained bridge head position may account for predominant cyclobutanol formation [99].

acetophenone (from Type II reaction) remains about constant as n increases from 3 to 7 despite the increasing stability of the cycloalkanone (the other Type II reaction product) in this series. However, the quantum yield of cyclization (to oxaspirane) decreases as n gets greater even though the reverse might be expected in view of the large amount of ring strain present in the oxaspirane when n is small. Again a steric effect explanation may be invoked : increasing the cycloalkyl ring size may increase its steric interactions with the phenyl and hydroxyl groups in the 1,4-biradical.

(d) 1,4-Biradicals and spin multiplicity effects on product formation

Two groups of investigators have tried to identify the initial state in which photoproducts form and hence make deductions about the existence and nature of the 1,4-biradical intermediate [103]. In both investigations 3,4-diphenylbutyrophenone ($PhCOCH_2CH(Ph)CH_2Ph$) which should produce cis- and trans-stilbene from the Type II reaction, was used. Both investigators showed by means of quenching studies that only the triplet was involved. In principle, there are three possible routes from the triplet reactant (or assumed triplet-derived 1,4-biradical) to form products in the ground state:

(I) via the excited singlet products to the ground state of the products

(II) via the triplet excited products to the ground state products

(III) straight to the ground state of the products.

It was considered on thermochemical grounds that the first alternative was unlikely but that the stilbene might be formed in the triplet state as the triplet excitation energy of the stilbene is less than that of both the enol of acetophenone (the other elimination product) and the

starting ketone *. In triplet stilbene, rotation about the C-C bond can occur and the trans:cis ratio should be 41:59 (from Hammond's work on the proportion of trans- and cis-stilbene from decay of triplet stilbene [106]). Caldwell and Fink who found the ratio to be 40:1, decided that most probably there is no intervention of stilbene triplets [103a]. Wagner and Kelso found that the ratio was 65:1 [103b] (subsequently Wagner and coworkers reported the initial ratio to be 70:1 [34]) and showed that the ratio dropped at higher conversions of the 3,4-diphenylbutyrophenone due to the sensitized isomerization of the initially formed trans-stilbene. (In Caldwell and Fink's experiment higher conversions were indeed obtained.) Now the Type II elimination of 3,4-diphenylbutyrophenone is estimated to be just exothermic enough to produce trans- and especially twisted-triplet stilbene [106] **. Therefore, these results [34,103] showed that little or no concerted reaction of the triplet ketone occurs and presumably

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* Both authors comment on the low quantum yield and short lifetime of the triplet of this ketone (quantum yield: 0,11 (benzene), 0,19 (2-methyl-2-propanol), reciprocal of lifetime: 2,1 $nsec^{-1}$), compared to butyrophenone (0,36, 0,85, 0,008 $nsec^{-1}$ respectively) [104]. β-Phenylbutyrophenone showed similar effects and a number of other authors have shown the low photochemical reactivity of compounds with β-phenyl groups [105]. Such peculiarities must be borne in mind in interpreting studies of these compounds.

** The calculations of Hoffman and coworkers showed no activation energy barrier to Type II cleavage of 1,4-biradicals [91a] while the thermochemical analysis of Benson and O'Neal gives an activation energy barrier of about 28kJ $mol^{-1}$ [91b].

the intermediacy of the 1,4-biradical is thereby implicated. It would then be reasonable to propose, in addition, that spin correlation in the 1,4-biradical is so weak (at least in these particular circumstances) that singlet-triplet distinctions are practically non-existent. Therefore, it appears that the 1,4-biradical then generates its products in their electronic ground states on fragmentation, the exothermicity of going to the ground state molecules possibly providing the driving force for fragmentation.

(c) 1,4-Biradicals and radiationless decay

On the basis of a variety of evidence, radiationless decay from both the singlet and triplet state is thought to occur by back-donation of the γ-hydrogen from the hydroxy group of the biradical to the γ-carbon radical site [28,88,107]. For example, in experiments using deuterated alcohols as solvents, small amounts of ketone were recovered with a deuterium atom at the γ-carbon site - presumably occurring through hydrogen-deuterium exchange between the solvent and the hydroxyl group of the 1,4-biradical, followed by back donation [99,108]. Another line of evidence is provided by Felt's report that thermal decomposition of 1,2-dimethylcyclobutanol gives some 2-hexanone and 3-methyl-2-pentanone [88] (see introduction, section D2(b)).

Yang has shown from measurements of intersystem crossing yields that, contrary to some earlier views [35,53,109], the singlet state in some cases may be responsible for far more radiationless decay than the triplet. In fact various authors' results with 2-pentanone show the ratio of radiationless decay:reaction is 11 to 14:1 for the singlet and about 1:1 for the triplet state [28,31,41]. However, it must be pointed out that the above calculation is based on the assumption that product formation and radiationless decay are the only two significant fates of these excited states.

The reason for this difference in behaviour of the singlet-derived and triplet-derived 1,4-biradical presumably lies with at least some of the same factors that affect the comparative stereoselectivity of their reactions (see Introduction, section D2(b)). For example, if Stephenson's calculations are correct and a lower rate of internal rotation is characteristic of the singlet-derived biradical [86b], then *it will remain for a longer period on average, in the conformation in* which it was initially generated. That conformation is presumably ideal for the back-donation of the γ-hydrogen and therefore radiationless decay is facilitated in the singlet biradical.

It is apparent that the nature of the γ-hydrogen affects the ease of intramolecular abstraction and therefore the proportion of singlet state molecules which undergo this abstraction in competition with intersystem crossing. Hence the total quantum yield of reaction will vary with the nature of the γ-hydrogen to a large extent because of the differing efficiencies of radiationless decay in the two states.

Steric hindrance to rotation in a 1,4-biradical as a cause of increased efficiency of radiationless decay, has been advocated by Golemba and Guillet [11] (see Introduction, section C3(b)), to explain the decreasing quantum yield of photoreaction with increased alkyl chain length in alkanones. They theorise that rotation away from the conformation in which the biradical is initially formed, is increasingly hindered by increasing the alkyl chain length.

## E The Role of the Solvent in Some Ketone Photoreactions

### 1. Hydrogen Transfer from Solvent and Other Molecules

Hydrogen transfer from solvent is an important reaction in regard to the fate of the radicals from Type I photodissociation and the-

excited state of the ketone itself. In this section both these processes will be briefly reviewed.

It has been known for a long time (Bamford and Norrish [2]) that the radicals from Type I fission abstract hydrogen from the solvent. These authors showed this by identifying the products from solvent radical disproportionation. Hartley and Guillet subsequently have proposed that the solvent radical combines with a second Type I radical or another solvent radical [9] (Scheme X). In a later paper Golemba and Guillet confirmed the latter but surprisingly disproportionation was not considered [11].

Scheme X

$$R_2CO \xrightarrow{h\nu} 2R^{\cdot} + CO$$

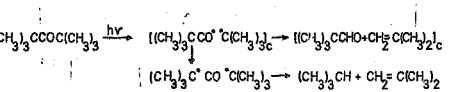
$$2R^{\cdot} + 2S\text{-}H \longrightarrow 2R\text{-}H + 2S^{\cdot} \longrightarrow S\text{-}S$$

In both of Guillet's papers, he reports finding no R-R [9,11]. However, many authors report finding products of Type I radical combination. Presumably the relative stability of R· and S· influence the outcome. This point was examined briefly in the present work.

It has also been shown that the radicals from Type I fission may abstract hydrogen from the parent ketone. For example, Ausloos and Paulson used a gaseous 1:1 mixture of acetone and deuterated acetone ($CD_3COCD_3$) and produced among other compounds some $CD_3H$ and $CH_3D$ [65], i.e. suggesting that hydrogen was abstracted from the ketone itself. More recently, in a study of the gas phase photolysis of 2,2,4,4,-tetradeutero-3-pentanone, Barto and Gordon showed that hydrogen (or deuterium) was abstracted from both the α or β positions of the ketone [110].

The significance of cage effects in regard to hydrogen abstraction by radicals from Type I fission in the liquid phase, has been shown by Cocivera and coworkers. These authors have made a CIDNP study of the hydrogen abstraction by 2-methyl-2-propyl radicals produced from di(2-methyl-2-propyl) ketone in perfluorocyclohexane solution [111]. They proposed the detailed scheme shown in Scheme XI.

Scheme XI



Numerous studies of hydrogen atom abstraction from solvents (HX) by the excited states of carbonyl compounds have been made (e.g. Walling and Gibian [54]). Such studies have led to the conclusion that this reaction is facilitated by: [32]

1. High electron density at the hydrogen atom abstracted
2. Low H-X bond strength
3. High stability of $X^{\cdot}$

Thus alcohols have the hydrogen from the alcoholic carbon abstracted by the oxygen atom of the excited carbonyl as in Scheme XII.

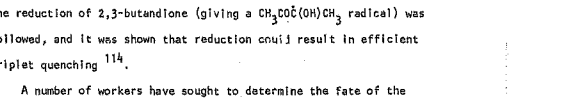
Scheme XII

Wagner has studied the reduction of acetone by hexane [112] and of acetone [25] and 2-hexanone [49] by tributyl stannane ($(1\text{-Bu})_3SnH$). He showed that in all these experiments only reduction of the triplet state occurred. Similar conclusions have been reached with regard to the photoreduction of many other ketones including 2-pentanone by hexane [28]. Thus the triplet state of alkanones is sufficiently reactive towards intermolecular hydrogen abstraction for this reaction to be competitive with radiationless decay.

E.s.r. spectroscopy has been used to establish the nature of the intermediate radical which results when the excited carbonyl compound abstracts a hydrogen atom from the solvent. In this way, for example, Yashida has identified the formation of $Ph_2\dot{C}OH$ in the photoreduction of benzophenone by ethanol [113]. In another experiment using e.s.r., the reduction of 2,3-butandione (giving a $CH_3C\dot{O}(OH)CH_3$ radical) was followed, and it was shown that reduction could result in efficient triplet quenching [114].

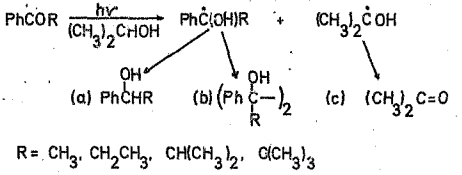
A number of workers have sought to determine the fate of the solvent radical derived from hydrogen abstraction by the excited carbonyl compound. In one of the earlier investigations of this type, Yang irradiated acetone and cyclohexane and found the result shown in Scheme XIII [3].

Scheme XIII



One of the most extensive product studies, is that of Lewis. He has observed the photoreduction of a number of α-substituted aryl alkyl ketones in 2M-2-propanol/benzene solvent [115] (Scheme XIV) and his findings are summarised below.

Scheme XIV




R = $CH_3$, $CH_2CH_3$, $CH(CH_3)_2$, $C(CH_3)_3$

(The pinacol (b) was obtained as a mixture of d, l and dl forms.)

(i) $\phi_c = \phi_b + \phi_a$ ($\phi$ = quantum yield)

(ii) $\phi_a$, $\phi_b$, $\phi_c$ α initial $[2P]$ (2P = 2-propanol)

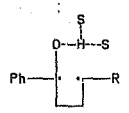
(iii) the rate constant for hydrogen abstraction by the triplet excited ketone decreases as R increases in size

(iv) $\phi_a$, $\phi_b$, $\phi_c$ decrease as R increases in size

(v) $\phi_a$: $\phi_b$ is constant over a range of values for $[2P]$

From (iii) and (iv) he concludes that there is a steric effect of α-substitutents (as has been seen in ground state reactions [116]) on hydrogen abstraction from solvents by excited carbonyl compounds. When R = $C(CH_3)_3$ only α-cleavage occurs although all four ketones studied exhibit essentially identical characteristic $n\pi^*$ emission spectra. Also there is no corresponding increase in the rate constant for triplet decay (from Stern-Volmer plots), i.e. the decrease in reactivity does not result from a shortened triplet life-

between the polar solvents and the OH group of the biradical retarded the return of the γ-hydrogen to the C atom from which it was abstracted [35,53] (i.e. the radiationless decay mechanism previously discussed).




Using solutions of a number of aryl alkyl ketones in benzene (or alkanes) to which increasing proportions of a polar solvent (2-methyl-2-propanol) were added, Wagner showed that in some cases the total quantum yield of reaction could be increased to near unity. For others, however, it levelled off at a maximum value somewhat less than this [35,43] *. The effectiveness of the different solvents used (pyridine, 2-methyl-2-propanol, tetrahydrofuran, ethyl acetate, dibutyl ether, butyronitrile, 1-chlorobutane [35,117]) paralleled their basicity rather than their dielectric constant or dipole moment.

Polar effects on quantum yields, though less dramatic, have also been observed for alkanones. For example, a two-fold increase of the total reaction quantum yield (based on ketone disappearance) for

---

* In the case of p-methoxyvalerophenone, increasing the proportion of polar solvent mixed with the benzene caused first an increase and then a decrease in quantum yields [43]. This was attributed to a change in character of the lowest excited state from predominantly $n\pi^*$ to predominantly $\pi\pi^*$.

2-pentanone has been recorded in going from benzene to 2-methyl-2-propanol [64]. A similar increase was observed by Wagner for 4-octanone [107] and 2-hexanone [49] in going from hexane to 2-methyl-2-propanol. It has also been shown that the selectivity [49] and quantum yield [49,64,107] of the triplet state of ketones both increase with increasing polarity.

As the ketone itself is a polar molecule, any increase in the ketone concentration should affect the polarity of the medium and hence have some effect on the quantum yield of reaction. Elliott found that an increase in 2-pentanone concentration actually decreased the quantum yield of reaction, there being a corresponding increase in the amount of radiationless decay [118]. Yang and coworkers observed a similar effect with acetone and showed that an excited and an unexcited ketone molecule may form an exciplex in this case, and that this provides an additional path of radiationless decay [119]. However, Wagner found that increasing the concentration of most aryl alkyl ketones, increased the quantum yield of reaction [117]. This is presumably due to the ketone acting as a Lewis base (hindering the γ-hydrogen return - as do polar solvents). Due to this effect any quantum yield determinations should be extrapolated to zero ketone concentration for purposes of comparison.

Barltrop and Coyle have found that polarity does not affect the elimination/cyclization ratio much in a series of aryl alkyl ketones [120] (actual figures are quoted only for dry $CH_3CN$ and benzene, however). With similar ketones, Wagner however, has noted in many cases that the proportion of cyclization drops when solvent polarity is increased (due to a decrease in cyclization rate) by changing from benzene to 2-methyl-2-propanol or wet $CH_3CN$ [35,75,96]. It would

appear as if the effect is small in aryl alkyl ketones and that it is detectable only by comparing the most polar with the least polar solvents. More pronounced effects have been reported with simple alkanones [64] (2-pentanone, 2-octanone and 5-methyl-2-hexanone). The singlet quantum yields of both cyclization and elimination were unaffected by solvent polarity changes but the triplet quantum yields were. The quantum yields of both reactions increased with increasing polarity, that of elimination increasing relatively more.

Wagner and coworkers have found furthermore that with the aryl alkyl ketones they used (above), the trans/cis ratio of the cyclobutanols formed decreased (towards unity) with increased solvent polarity [96]. They explain all these phenomena by suggesting that solvation:

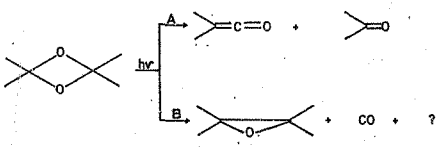
(i) prevents the γ-hydrogen return in the triplet-derived biradical, thus increasing the total quantum yield of triplet reaction

(ii) increases the bulk of the hydroxyl group so that cyclization is hindered and the steric difference between the cis- and trans-cyclization transition states is diminished.

The behaviour of γ- and δ-alkoxyvalerophenone in different solvents [96] provides supportive evidence for the feasibility of such an explanation.

Finally attention must be drawn to a remarkable solvent polarity effect on the competing pathways of photoreaction of tetramethyloxetanone [121] (Scheme XV over).

Scheme XV




The two reactions both occur from the excited singlet state but reaction A is enhanced at the expense of the reaction B in the more polar solvents (alcohols versus hydrocarbons). Wagner and coworkers suspect this observation may be related to the solvent effects on competing alkoxy radical reactions noted earlier by Walling and Wagner. *These authors consider that polar solvents preferentially* lower the energy of the transition state for alkoxy radical fragmentation as opposed to that for hydrogen atom abstraction from substrate molecules [122]. A similar effect might be expected upon the competition between elimination and cyclization of 1,4-biradicals in ketone photochemistry and indeed the increase in the proportion of elimination with respect to the cyclization with increasing polarity, which was noted above [35,64,75,96], may be a related phenomenon.

3. Solvent Viscosity Effects

Effects of medium viscosity on photochemical events of interest to the present work have only been sporadically reported [123,124,125,126]. There are well-documented examples relating to bimolecular reactions (including energy transfer) of excited states where viscosity effects on the diffusion of the molecules occurs. However, the only bimolecular reaction in the present work is photoreduction by hydrogen

abstraction from solvent which of course does not involve diffusion by either species.

Reports of viscosity effects on unimolecular events involving ketones relate primarily to the Type I reaction. The effects are expected to be comparable to those observed in other homolytic dissociations. Other effects have been studied so little that it is necessary to consider the photochemistry of compounds other than ketones to gain an impression of their possible significance.

(a) Influence of the solvent on diffusion:solvent cage effect

As mentioned above this primarily concerns Type I reactions. Solvent cage effects were first noticed in 1934 [127]. It is currently believed that they can be estimated by suitable interpretation of results from experiments with scavengers and that their magnitude is related to solvent viscosity. Much work has been done on cage effects with compounds that easily produce radicals, thermally or photochemically, e.g. azo compounds and peresters [128]. However, comparatively little work has been done on the cage effect with respect to the photolysis of ketones. The quantum yields of Type I reaction products, and in a more indirect way Type II and cyclization products may well be affected by the magnitude of the cage effect and hence be viscosity dependent.

As radical-radical recombinations are fast enough to compete with diffusion, but the diffusion rate depends on viscosity, a lower rate of product formation from homolysis of an initiator might be expected for high viscosities of the medium. Pryor and Smith have argued, however, that there need not always be an interrelationship between the rate of product formation and medium viscosity [129]. When a radical pair is formed by fission of a single bond in the initiator, the cage

effect causes regeneration of the starting material. In such cases, therefore, solvents which increase the cage effect, reduce the overall rate of product formation. However, initiators undergoing concerted fission of two bonds (or a stepwise fission in which the second bond breaks very rapidly) forming a radical pair and a stable (intervening) molecule, are not regenerated by the cage effect and *solvents will have no effect on the rate of product formation.* A few studies of the relation between Type I reaction quantum yields and solvent viscosity have been reported, in which differing hydrocarbon solvents were used. In these Hartley and Guillet showed that there is little effect on Type I quantum yields for hydrocarbon solutions of 1,4-polyphenylene-carbon monoxide copolymer [130] and linear symmetrical alkanones [9]. Subsequently, however, Goiemba and Guillet have shown a significant reduction of Type I quantum yields with increasing viscosity in the case of long chain 2-alkanones at temperatures below 120°C [11]. Above 120° no viscosity effect was observed. In all these studies, Guillet and coworkers found that the Type I quantum yield was markedly increased by increasing temperature.

Guillet and coworkers, in another paper, have invoked the cage effect to explain their observation that the smaller sidechain of a ketone may be cleaved off in a Type I (radical) reaction in solution, in preference to a large sidechain [16]. They suggest that the surrounding cage may allow the smaller radical to escape more easily after dissociation *. There may be a connection here with the

---

* They also suggest that the cage recombination of Type I fragments may provide a mechanism for radiationless decay of ketones in solution.

different viscosity dependences of Type I quantum yields observed in their work using different types of ketones.

The totality of these results seems to be most economically accommodated by regarding the Type I reaction as a two step one wherein the second step occurs at a rate that depends on the nature of the acyl radical (and the alkyl radical formed by decarbonylation - Scheme XVI), and the temperature.

Scheme XVI

$$R_1COR \xrightarrow{h\nu} R_1^{\bullet} + {}^{\bullet}COR \longrightarrow R_1^{\bullet} + CO + {}^{\bullet}R$$

There may also be a spin multiplicity effect. Thus, in a two step decomposition mechanism, if the recombination of the first pair of radicals is retarded because they have the same spins, then their pair lifetimes may be such that either they will always be able to diffuse part (whatever the solvent viscosity) or the second bond will always break before recombination of the first pair can occur. This may be a factor operative in the triplet photodecarbonylation of dibenzyl ketone [45].

(b) Influence of the solvent on internal motions

A number of scattered reports of viscosity effects on photochemical events have recently been correlated and reviewed by Saltiel and D'Agostino [123]. Their own work concerned viscosity effects on the fluorescence and photoisomerization of stilbenes - a phenomenon also extensively studied by Fischer, Muszkat and coworkers [124].

At low solvent viscosities no effect is observed but as the viscosity is progressively increased, an effect develops: the quantum yield of fluorescence increases and that of isomerization (by internal rotation) decreases. Saltiel and D'Agostino suggest that if solvent mobility is fast (low-viscosity) relative to the rate of the internal rotation then no "interference" by the solvent is detectable [123]. If, however, the rate of solvent relaxation is comparable to or less than that of the internal rotation, then the rotation becomes a cooperative event and an activation energy greater than the intrinsic value is observed. In these circumstances a viscosity dependence arises.

Other reports of viscosity effects on fluorescence quantum yields have also appeared [125]. With one exception the effects could be attributed to the viscosity influence on the rate of a competitive radiationless decay process which involved some change of molecular geometry by bond rotation, etc.*.

The situation with regard to triplet state phenomena is less clear. The greater lifetime of this state has led Saltiel and D'Agostino to suggest that the few viscosity effects reported may not be kinetic phenomena but equilibrium ones [123]. They suggest that in viscous media there may be a preference for conformations of minimum volume and that this may be the underlying explanation of these phenomena.

An alternative analysis of the effect of viscosity on the competition between fluorescence and photoisomerization of stilbenes

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* The one exception involved competition with intersystem crossing to an excited triplet ($T_2$) state.

to increased probability of that γ-hydrogen abstraction which leads ultimately to formation of the higher energy alkene. In less viscous media, conformational equilibration is comparatively rapid and so the lower energy alkene is preferentially formed via the transition state of lowest energy. Similar effects had been reported by Borkowski and Ausloos much earlier in their study of the photolysis of 2-butyl acetate [131]. However, the effects attributed to viscosity variance were induced by temperature variance of the reaction system (down to -195°) and their interpretation at the time was thereby rendered rather less certain.

No work on the relation between the efficiency of cyclobutanol formation and medium viscosity seems to have been reported. However, Guillet and coworkers reported a brief study of the relation of the quantum efficiency of the Type II reaction of a variety of ketones to viscosity of the solvent [9,11]. They found no viscosity effect and very little temperature effect.

F Aims of the Present Experimental Work

The principal aim of the present work was to study effects of solvent variation on the relative proportion of Type II photoelimination and cyclization. As already shown, there is a certain amount known about the comparative effects of hydrocarbon and alcohol solvents (see Introduction, section E2), and the object of this work was to try and expand understanding of these effects by studying a wider range of these solvents. In addition, solvent viscosity effects had been little investigated and seemed to be of potential interest.

It was difficult to predict the nett effects on the elimination and cyclization reactions, in view of the many rate processes which influence the quantum yield of these reactions (e.g. nature of excited

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states participating (introduction, section C3(b)), rate of internal rotation in the 1,4-biradical (introduction, sections D2(c) and E3(b)) and solvation of the 1,4-biradical (introduction, section E2)). However, taking the simple view of possible viscosity effects, it seemed possible that the cyclization might be increasingly favoured over elimination with increasing solvent viscosity. The rationale was that the greater the viscosity of the solvent, the more favourable should be the transition state of lower volume, i.e. the transition for cyclization which leads to one molecule.

In any event, the results seemed likely to be not only of fundamental photochemical interest, but also possibly of practical synthetic value.

has been presented by Fischer and coworkers [124c]. Some of the basic features of their analysis are similar to those of Saltiel and D'Agostino, but according to the latter authors, it has a number of shortcomings [123].

Brown has also reported effects of solvent viscosity on the photochemistry of 2-pentylphenyl acetate and 2-pentyl benzoate [126]. Esters undergo a Type II cleavage reaction as do ketones, though a shorter wavelength of radiation is required. Two principal effects of interest were observed. Firstly, the Type II reaction quantum yield decreased with increasing viscosity, an effect attributed to the increasing efficiency of γ-hydrogen back-donation in the 1,4-biradical. Brown suggests that increasing solvent viscosity * retards internal rotation in the 1,4-tiradical so that the conformation in which the 1,4-biradical is formed (and which is ideal for return) is maintained on average for longer. Secondly, the proportions in which the alternative Type II elimination products (1-pentene and 2-pentene) were formed showed variance with solvent viscosity at high viscosities. Interpreting this, Brown noted that the lowest energy ground state conformation led (by γ-hydrogen abstraction) to the higher energy alkene. Since the proportion of the higher energy alkene increased at high viscosities, Brown postulated that the lowest energy ground state conformation was maintained for longer on excitation and so led

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* The effect was studied principally using a series of alcohols. Comparison of quantum yields in 2-methyl-2-propanol and hexadecane which have similar viscosities, indicated no solvent polarity effect. This is consistent with the fact that photolysis of these esters occurs predominantly from the singlet state.

# EXPERIMENTAL

A. The Origin, Preparation and Purification of Starting Materials and Products

1. Starting Materials

(a) Ketones

Samples of the three ketones studied were all of analytical grade quality and were used without further purification. Their origin was as follows:

| | |
|---|---|
| 2-pentanone (99%) | - Hopkins & Williams |
| 2-hexanone (> 99%) | - Fluka |
| 4-methyl-2-pentanone (98%) | - BDH |

The 2-pentanone was at least 99% pure as shown by gas chromatography. This was in accord with the supplier's claim. However, Calvert and Pitts have reported [32] that there may be substantial amounts of 3-pentanone present in 2-pentanone. As a mixture of these two is very difficult to resolve by gas chromatography, an infrared spectrum of the 2-pentanone was compared with literature spectra of 3-pentanone [132]. The conclusion reached was that if any 3-pentanone was present, it was only in trace amounts. This was confirmed in a letter from Hopkins & Williams.

(b) Solvents

A list of the solvents used and their origin is given below. No further purification of the purchased materials was carried out except that the decanol and 1,2-propandiol were redistilled:

| | | |
|---|---|---|
| "Nujol" | - | Rexall (medicinal paraffin) |
| 1-Decanol | - | L. Light (unspecified quality) |
| Methanol, Ethanol | - | E. Merck (analytical reagent) |
| 2-Methyl-2-propanol | - | E. Merck (commercial purity) |
| 1-Octanol, 1,2-Ethandiol, Cyclohexanol | - | E. Merck (unspecified quality) |
| Hexane | - | BDH (for chromatography) |
| Dodecane, Hexadecane, 2-Propanol, 1-Heptanol, 2-Octanol, 1,2-Propandiol, Dodecanol | - | BDH (unspecified quality) |
| 2-Heptanol, 2,6-Dimethyl-4-heptanol | - | Prepared by reduction of the corresponding ketone using a large scale version of the method described in the next section (Experimental, section A2(a)) with 65% and 50% yields respectively. |

Other solvents were tried but discarded for one or more of the following three reasons:

(i) The solvent peak obscured the acetone or cyclobutanol peaks on the gas chromatogram under all convenient operating conditions (1-propanol, 2-butanol, 2-butanol, 2-pentanol, 2-hexanol, decane).

(ii) Impurities which could not be removed by repeated distillations obscured certain products (1-pentanol).

(iii) The generation of a yellow colour on exposure to radiation which apparently impeded any further photochemical change of the ketone. The colour could be removed by distillation but was regenerated on further irradiation (1-hexanol, 1,3-propandiol, benzyl alcohol).

2. Photoproducts

(a) Alcohols

On the basis of gas chromatographic experiments and literature reports one of the photoproducts was expected to be the reduced ketone. Thus samples were needed to test this suggestion. The alcohols 2-pentanol and 2-hexanol were both commercially available, but 4-methyl-2-pentanol was not and was prepared as follows:

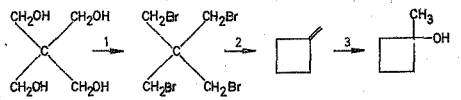
Sodium borohydride (2g) was slowly added to 4-methyl-2-pentanone (7,5g) in methanol (10 ml), adding more methanol when necessary (the reaction was exothermic and effervescent). When addition was complete, the mixture was refluxed for 10 minutes, and then water (8 ml) and 2M hydrochloric acid (10 ml) was added. It was then refluxed for a further 10 minutes. Sodium chloride was added to saturate the aqueous layer which was then extracted with ether (3 x 30 ml). The ether solution was dried and the solvent removed. As the sample was required for qualitative comparisons only, no further purification was attempted.

(b) Cyclobutanols

A sample of cis-1,2-dimethylcyclobutanol was kindly supplied by Dr E.D. Felt of Bell Laboratories, U.S.A. [88].

Two methods of preparation of 1-methylcyclobutanol were attempted.

Procedure A : The method that was adopted is outlined below:



Step 1

The method reported in Organic Syntheses [133] was used to prepare the pentaerythritol tetrabromide. The crude product (73%) was used without further purification.

Step 2

The procedure followed was a combination of two previously reported methods [134,135]. The crude tetrabromide (250g), powdered zinc (250g), ethanol (20 ml) and zinc bromide (7g) were placed in a three-necked 5 ℓ flask fitted with a dropping funnel, a mercury-sealed stirrer and a collecting unit. This unit consisted of two water-cooled condensers leading to a receiver cooled in dry ice and fitted with a $CaCl_2$ tube. At a temperature of 85°C, water (500g) was slowly added via the dropping funnel and the vigorous reaction regulated by means of the rate of stirring. When the addition was complete, the temperature was raised to 90°C for half an hour to drive over any remaining methylenecyclobutane. Further purification was not attempted and the yield of crude material was estimated at 60%.

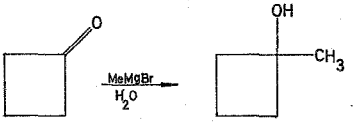
Step 3

Two reports mentioned the addition of 66% sulphuric acid to methylenecyclobutane for the hydration step but no experimental details were given [135,136]. The following procedure was found to be satisfactory.

The acid (80 ml) was added to the crude methylenecyclobutane (40 ml) and the mixture was held at 5-10°C in a refrigerator overnight. It was extracted with ether (3 x 50 ml) taking care to maintain the temperature below 20°C. (If the temperature rose above this value, a black tar resulted.) The mixture was returned to the refrigerator and a further extraction (2 x 50 ml) was done on each of the two following days. The combined ether extracts were dried and most of the solvent removed. The yellow impurity was removed by column

chromatography with pentane/ether followed by microdistillation. The i.r. spectrum of this material was indistinguishable from that of 1-methylcyclobutanol obtained from procedure B, but the mass spectrum of the compound showed that a significant amount of a bromine-containing impurity was present. Despite extensive efforts this impurity could not be removed. The impure 1-methylcyclobutanol prepared in this way was used for qualitative work only.

Procedure B : A method which was found to be more satisfactory is outlined below:




Methyl bromide (20g, 0,21 mol) was dissolved in dry ether (100 ml) at 0°C. The solution was slowly added via a dropping funnel to magnesium ribbon (4,8g, 0,20 mol) in dry ether (50 ml). A crystal of iodine was added to initiate the reaction. The rate of addition of the methyl bromide solution was adjusted so as to keep the reaction mixture just refluxing. When the addition was complete it was allowed to stand for 30 minutes. To the flask with the Grignard reagent, was added a solution of cyclobutanone (Fluka) (5g, 5,5 ml, 0,07 mol) in dry ether (10 ml) at a rate sufficient to maintain the mixture refluxing. It was allowed to stand for 15 minutes and then poured onto ice (700g). To this was added 10% sulphuric acid (100 ml). The two layers were seperated and the aqueous acid layer further extracted with ether (2 x 100 ml). The organic layers were then combined and dried over anhydrous potassium carbonate. After removal

of the solvent, the 1-methylcyclobutanol was distilled under reduced pressure to yield a colourless liquid (4g, 65%) which gave a single peak on the gas chromatograph (FFAP column) and showed the following spectral characteristics:

i.r. (liquid film; $\nu_{max}$ 3330 (s,OH), 2950, 2800, 1450, 1365, 1200, 1170, 1150 (m,OH), 950 $cm^{-1}$); n.m.r. (TMS, $CCl_4$, $\delta$ 1,33 (s, 3H, $CH_3$), 1,91 (m, 6H), 4,33 (s, 1H, exchange with $D_2O$, OH)).

The mass spectrum showed the molecular ion at m/e 86 and was in accord with that quoted in the literature [14].

(c) Ketals

Samples of the two dioxolanes derived from reaction of 1,2-ethandiol with acetone (2,2-dimethyl-1,3-dioxolane) and with 2-pentanone (2-methyl-2-propyl-1,3-dioxolane) were kindly supplied by Mr J.P. Michael of these laboratories.

2,2-Dimethoxypropane was purchased from E. Merck & Co., while a sample of 2,2-dimethoxypentane was kindly supplied by Mr F. Knoth of these laboratories.

B. Method of Irradiation

0,23M Solutions of the three ketones used were all irradiated in 10 ml pyrex volumetric flasks. The solutions were prepared in the flasks by adding the desired amount of ketone with a syringe and making up to 10 ml with the required solvent. The air volume remaining above the graduation was protected with aluminium foil to avoid complications due to irradiation of the ketone vapour. The irradiations were carried out for 20 1/4 hours on an air-cooled roundabout apparatus (Fig. 2). Samples were clamped at a fixed distance from the medium-pressure mercury light source (Hanau). The temperature of the samples during irradiation depended on the surrounding temperature and ranged from 23° to 27°C.

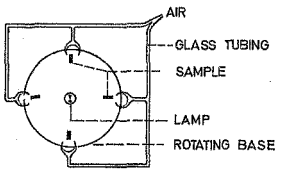



Figure 2 : View from above of irradiation apparatus

C. Method of Analysis

A Perkin-Elmer Model 880 gas chromatograph (g.c.) fitted with a dual flame ionisation detector was used. Two columns were made using $^1/8$ inch diameter stainless steel tubing. One, a 6ft column, was packed with FFAP, a packing of medium polarity of the Carbowax type (10% on Chromsorb Q), while the other, a 12ft column, contained Apiezon L (15% on Celite). Reference samples of the ketones and the two main products of interest (acetone and cyclobutanol) were run to establish the best operating conditions. The chosen conditions were as follows: The helium pressure was 30 $lb/in^2$ giving a flow rate of about 30 ml/min. The FFAP column was programmed from 50 to 150°C at six degrees/minute, the Apiezon L column from 60 to 160°C at four degrees/minute. The initial injector temperature was 70° in both cases.

Most of the quantitative data were obtained with the FFAP column. The Apiezon L column was used for quantitative analysis only for reaction mixtures from photolyses of 2-pentanone in hydrocarbon solvents (due to

the keto ), cyclobutanol or reduced ketone peaks merging with each other). However, it was also used in qualitative investigations into the nature of other products (see below and Experimental, section F). Each irradiation of a sample is described as a photolysis while the description "chromatogram" implies one injection (or analysis) of the sample. Each sample was run on the g.c. within twelve hours after irradiation. This was due to the fact that in 2-pentanone photolysates, the two peaks assigned to 2-propanol and 2-pentanol increased, while those assigned to acetone and 2-pentanone decreased with time in hydrocarbon solvents (evident after four days storage in darkness). This did not appear to happen for alcohol solvents - but nevertheless all photolyses were analysed within twelve hours. No experiments were done to investigate the cause of this effect.

The assignments of the peaks on the g.c. traces of the three irradiated ketones were done in most cases on the basis of comparison with authentic samples on both columns (acetone, 2-propanol, 2-pentanone, 2-hexanone, 4-methyl-2-pentanone, 2-pentanol, 4-methyl-2-pentanol, 2 hexanol, 1-methylcyclobutanol, cis-1,2-dimethylcyclobutanol). In the case of trans-1,2-dimethylcyclobutanol and cis and trans-1,3-dimethylcyclobutanol, where authentic samples were not available, assignments were made by referring to the position of the cis-1,2-dimethylcyclobutanol. The cis and trans-1,3-dimethylcyclobutanols (from 4-methyl-2-pentanone) appeared to be unresolved in some chromatograms and partially resol[illegible]ers and, other than a peak corresponding to an impurity [illegible]yl-2-pentanone, it was the only peak of retention time rough[illegible]he area expected for dimethylcyclobutanols. The trans-1,2-dimethylcyclobutanol, if resolved from the cis isomer, would be expected to have a shorter retention time

than the cis isomer [96]. A small peak was observed in this region and was assigned to the trans isomer.

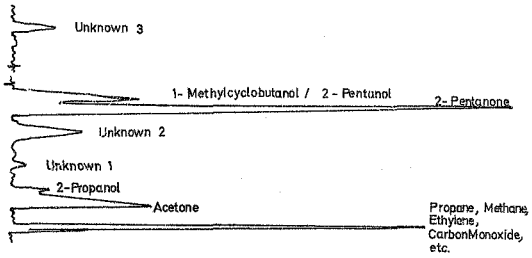
D. Results of Photolyses

Since the principal objective of this work was to determine trends in the relative yields of acetone and cyclobutanol, it was felt that measurement of a ratio of peak heights would be sufficiently accurate. All figures quoted are the average of the figures for all photolyses of that system (e.g. 2-pentanone in hexane) while the figure for each photolysis is in turn the average of that obtained from several (two to four) chromatograms. Differences in the peak heights of individual components in different chromatograms were usually found to be small. These differences are presumably due to a failure to reproduce precisely the g.c. analysis conditions and/or the injections. On the other hand comparisons of peak heights for individual components in different photolyses sometimes showed differences as great as about 25% although they were usually much less than this. In six solvents, two distinct sets of peak height averages from different photolyses were obtained and these were both recorded. These differences were presumably due to differences in photolytic conditions, e.g. lamp output, distance between lamp and sample.

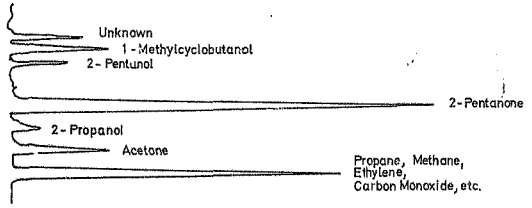
The response of the g.c. detector to the three compounds of interest, was checked by means of a number of carefully prepared standard solutions. The ratio of the responses to acetone : 2-pentanone : 1-methylcyclobutanol (determined with solutions of concentrations comparable to those obtained in the photolysis mixtures), was 1,3:1,2:1,0. In view of the fact that the work was only intended to be semi-quantitative in nature, it was felt that the error incurred by neglecting these slight differences was too small to be important and

would be unlikely to obscure any trends. Thus the peak heights were not corrected for detector response.

To give an impression of the appearance of gas chromatograms obtained with the two different columns, two examples are included in Figure 3. Both are of the reaction mixture from the photolysis of 2-pentanone in hexadecane. Tables I to V (following) list the results in terms of average peak heights on the chromatograms of photoreaction mixtures of the three ketones used. For all the tables, the peak heights correspond to a g.c. attenuation of 200 (unless stated) with a Hitachi QPD53 recorder showing a full scale deflection at 5mV being used.




Apiezon L column




FFAP column

Figure. 3: Specimen chromatograms of 2-pentanone in hexadecane

Table I 2-Pentanone : Average peak heights (cm) of components of irradiated solutions as determined on FFAP column

| Solvent | Acetone | 2-Propanol | 2-Pentanone | 2-Pentanol | 1-Methyl-cyclo-butanol | Unknown (retention time 9,8min) | Total component peak heights | Number of photolyses |
|---|---|---|---|---|---|---|---|---|
| Hexane | 4 [a] | 1,2 [a] | 9,6 | 1,5 [a] | 3,6 [a] | 1,8 | 21,7 | 7 |
| | 10,2 [a] | 1,8 [a] | 22,1 | b | 11 [a] | 3,8 | 48,9 | 1 |
| Dodecane | 6,6 | 1,2 | 19,8 | 2,8 | 5,2 | c | 35,6 | 2 |
| Hexadecane | 4,4 | 1,5 | 13,5 | 2,6 | 4,2 | 2,9 | 29,1 | 2 |
| "Nujol" | 2,4 | b | 10,8 | 2,5 | 2,3 | 2,4 | 20,4 | 4 |
| Methanol | 17,1 | b | 17,4 | 1,1 | 10,0 | 0,6 | 46,2 | 2 |
| Ethanol | 6,7 | b | c | 9,3 | 5,5 | 5,0 | - | 4 |
| 1-Heptanol | 10,0 | 1,9 | 21,2 | 10,0 | 8,8 | c | 51,9 | 2 |
| 2-Octanol | 12,9 | 2,1 | 26,9 | 9,8 | 4,9 | 4,9 | 61,5 | 2 |
| 1-Decanol | 10,5 | b | 25,3 | 7,3 | 7,4 | 6,2 | 55,7 | 4 |
| 1,2-Ethandiol | 3,4 | b | 13,7 | 7,5 | 7,0 | 6,2 | 37,8 | 2 |
| 1,2-Propandiol | 9,3 | b | 33,9 | 6,5 | 5,2 | 5,4 | 60,3 | 2 |
| 2-Methyl-2-propanol | 20,5 | b | b | 0,3 [a] | 13,3 | 0,3 [a] | - | 1 |

a) approximate measurement

b) peak height was not measured as peak was not sharp enough

c) not measurable as peak was obscured by solvent

Tabl. II 2-Pentanone-additional solvents: Average peak heights (cm) of components of irradiated solutions as determined on FFAP column

| Solvent | Acetone | 2-Propanol | 2-Pentanone | 2-Pentanol | 1-Methyl-cyclo-butanol | Unknown (retention time 9,8min) | Total component peak heights | Number of photolyses |
|---|---|---|---|---|---|---|---|---|
| 2-Propanol | 18,3 | b | b | 14,7 [c] | 4,8 | 2,7 | - | 3 |
| 2-Heptanol | 11,3 | 2,3 | d | 13 [c] | 7,3 | b | - | 1 |
| 1-Octanol | 9,6 | 1,6 | 25,2 | 9,1 | 7,8 | 8,6 | 61,9 | 1 |
| Cyclohexanol | 3,5 | 0,1 [c] | 54,7 | 10,1 | 1,6 | 1,8 | 71,8 | 1 |
| 2,6-Dimethyl-4-heptanol | 13,2 | 1,5 | 21,0 | 3 [c] | 10 [c] | 4 [c] | 52,7 | 2 |
| 1-Dodecanol | 6,6 | 0,8 | d | 6,0 | 5,7 | 5,7 | - | 2 |
| 1,3-Propandiol [e] | 1,0 | a | 96,5 | 1,3 | 1,5 | 0,1 | - | 1 |
| Benzyl alcohol [e] | 0,5 | a | d | 1,9 | 0,4 [a] | a | - | 1 |

a) peak height was not measured as peak was not sharp enough

b) not measurable as peak was obscured by solvent

c) approximate measurement

d) not measurable as peak was off-scale

e) measured at low attenuation and corrected to standard attenuation.

Table III 4-Methyl-2-pentanone: Average peak heights (cm) of components of irradiated solutions as determined on FFAP column

| Solvent | Acetone | 2-Propanol | 4-Methyl-2-pentanone | 1,3-Dimethylcyclobutanol (2 isomers) | Total component peak [a] heights | Number of photolyses |
|---|---|---|---|---|---|---|
| Hexane | 14 [b] | c | 18,6 | 4,7 | 37,3 | 2 |
| | 11,2 | c | 22,8 | 2,4/0,8 | 37,2 | 1 |
| Dodecane | 10,0 | 1,2 | 23,1 | 2,0/0,7 | 37,0 | 2 |
| Hexadecane | 10,6 | 1,4 | 28 [b] | 2,5/0,1 | 42,6 | 1 |
| "Nujol" | 6,8 | 1,5 | 22 [b] | 3,5 | 33,8 | 1 |
| Methanol | 16,1 | c | 18,8 | 1,6/0,9 | 37,4 | 1 |
| | 18,0 | c | 20 [b] | 1,6/1,0 | 40,6 | 1 |
| Ethanol | 11,6 | c | 11 [b] | 4,3/4,6 | 31,5 | 1 |
| | 19,5 | 1,5 | 19,9 | 2,7/3,3 | 46,9 | 1 |
| 1-Heptanol | 14,3 | 2,5 | 11,8 | 6,7/1,0 | 36,3 | 1 |
| | 16,8 | 1,7 | 26,7 | 5,0/1,1 | 51,3 | 1 |
| 2-Octanol | 16,8 | 1,5 | 34,0 | 1,9/0,4 | 54,6 | 2 |
| 1-Decanol | 17,4 | 2,1 | 22,4 | 5,4 | 47,3 | 2 |
| 1,2-Ethandiol | 3,6 | c | 15,7 | d | 35,3 [e] | 1 |
| 1,2-Propandiol | 12,0 | 1,1 | 20,5 | 3,7 [b] | 37,3 | 1 |

a) total excludes any reduced ketone (4-methyl-2-pentanol) as this peak coincides in retention time with an impurity in the 4-methyl-2-pentenone

b) approximate measurement c) peak height was not measured as peak was not sharp enough d) small

e) includes 16 cm for 2 peaks (possibly ketals)

Table IV 2-Hexanone: Average peak heights (cm) of components of irradiated solutions as determined on FFAP column together with % yields of 2-hexanol as determined on Apiezon L column.

| Solvent | Acetone | 2-Propanol | 2-Hexanone | trans-1,2-Dimethyl-cyclo-butanol | cis-1,2-Dimethyl-cyclobutanol (+ 2-Hexanol) | Total component peak heights | Number of photolyses | 2-Hexanol [a] % | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | of components | of products |
| Hexane | 11 [b] | c | 43,5 | 5 [b] | 4,9 | 64,4 | 1 | 1,8 | 4 |
| Dodecane | 7,5 | 0,5 | 35,1 | 3,7 [b] | d | 46,8 | 1 | 1,1 | 4 |
| Hexadecane | 11,2 | 0,8 | 44,4 | 4,6 | 3,8 | 64,8 | 1 | 1,0 | 4 |
| "Nujol" | 6,9 | 0,7 | 36,7 | 3,5 | 3,7 | 51,5 | 1 | 1,2 | 6 |
| Methanol | 10,7 | c | 34,0 | 4 [b] | 3,2 [b] | 51,9 | 1 | 0,4 | 1 |
| | 19,9 | c | d | 4,5 | 3,6 | - | 1 | | |
| Ethanol | 12,1 | c | 35,9 | 4,3 [b] | 4,0 [b] | 56,3 | 1 | 1,2 | 5 |
| 1-Heptanol | 14,4 | 1,8 | 50,5 | 6,2 | 5 [b] | 77,9 | 1 | | |
| 2-Octanol | 13,2 | 1,0 | 53,8 | 3,2 | 3,2 | 74,4 | 1 | 0,2 | 0,4 |
| Decanol | 13,0 | 1,7 | 49,5 | 4,6 | 4,5 | 73,3 | 1 | 0,8 | 4 |
| 1,2-Ethandiol | 3,2 | 0,4 | 28,6 | 4 [b] | 3,2 | 45,6 [e] | 1 | | |
| 1,2-Propandiol | 5,7 | 0,8 | 35,3 | 2 [b] | 2 [b] | 45,8 | 1 | | |
| 2-Methyl-2-propanol | 10,5 | c | d | 3,2 | 2,7 | - | 1 | | |

a) estimates from Apiezon L column

b) approximate measurement

c) peak height not measured as peak was not sharp enough

d) not measurable as peak was obscured by solvent

e) includes 6,2 cm for 2 peaks (possibly ketals)

*Table V* *2-Pentanone: Average peak heights (cm) of components of Irradiated hydrocarbon solutions as determined on Apiezon L column*

| Solvent | Acetone | 2-Propanol | Unknown 1 (retention time 5,5min) | Unknown 2 (retention time 7,3min) | 2-Pentanone | 1-Methyl-cyclobutanol + 2-Pentanol | Unknown 3 (retention time 17,5min) | Total component peak heights |
|---|---|---|---|---|---|---|---|---|
| Hexane | 9,0 | 2,0 | b | b | b | 6,4 [a] | 1,6 | - |
| *Dodecane* | 4,4 | 0,5 | 0,7 | 1,6 | 10,4 | 3,4 | 1,4 | 22,4 |
| Hexadecane | 5,6 | 0,7 | 1,2 | 2,6 | 21,2 | 5,1 | 2,2 | 38,6 |
| "Nujol" | 3,6 | 0,4 | 0,7 | 2,0 | 16,1 | 3,6 | 1,9 | 28,3 |

a) approximate measurement

b) not measurable as peak obscured by solvent

E. Quenching Studies

Table VI contains the results of photolyses in which the quencher cis-1,3-pentadiene was present. Due to the low conversions in these photolyses the peak heights in Table VI are less reliable than those of previous tables.

Table VI Ketones irradiated with cis-1,3-pentadiene (13 PD) : Heights of two main product peaks (cm) [a] - average from chromatograms of one long-term) photolysis

| Solvent | Ketone [b] | 13 PD | Acetone | Substituted cyclobutanol |
|---|---|---|---|---|
| "Nujol" | 2P | - | 33,4 | 32,4 |
| | 2P | 0,15M | 4,4 | 0,8 |
| | 4M2P | 0,15M | 10,1 | c |
| | 2H | 0,15M | 21,6 | 9,6 |
| 1,2-Ethandiol | 2P | - | 7,6 | 15,6 |
| | 2P | 0,15M | 9,5 | 1,3 |
| | 4M2P | 0,15M | 11,6 | c |
| | 2H | 0,15M | 33,2 | 8,8 |
| Methanol | 2P | - | 58,0 | 38,8 |
| | 2P | 0,15M | 2,6 | 3,5 |
| | 4M2P | 0,15M | 5,5 | c |
| | 2H | 0,15M | 19,6 | 21,4 |
| 2-Octanol | 2P | - | 25,2 | 10,0 |
| | 2P | 0,15M | 18,9 | 1,6 |
| | 4M2P | 0,15M | 10,3 | c |
| | 2H | 0,15M | 32,8 | 7,6 |
| Hexadecane | 2P | 0,15M | 12,8 | 1,9 |
| Ethanol | 2P | 0,15M | 12,2 | 4,1 |
| Cyclohexanol | 2P | 0,15M | 7,8 | 1,9 |

a) g.c. attenuation at 50

b) 2P = 2-pentanone, 2H = 2-hexanone, 4M2P = 4-methyl-2-pentanone

c) small

For purposes of comparison, a number of short-term irradiations in the absence of quencher were performed. The period of photolysis (about three hours) was chosen to produce approximately the same amount of cyclobutanol as was formed in the experiments with cis-1,3-pentadiene present. The results of such photolyses are recorded in Table VII.

Table VII 2-Pentanone: 3 hour irradiations. Heights of two main product peaks (cm) [a] - average from chromatograms of one photolysis

| Solvent | Acetone | 1-Methylcyclobutanol |
|---|---|---|
| Hexane | 5,5 [b] | 3,3 [b] |
| Hexadecane | 10,9 | 8,6 |
| Methanol | 11,1 | 6,5 |
| Ethanol | 10,3 | 5,4 |
| 1-Heptanol | 8,8 | 7,2 |
| 2-Octanol | 9,6 | 3,4 |
| 1-Decanol | 19,7 | 6,0 |
| Cyclohexanol | 4,1 | 3,2 |
| 1,2-Propandiol | 6,5 | 3,5 |

a) g.c. attenuation at 50

b) approximate measurement

F. Additional Products

G.c. investigation of photoreaction mixtures showed that they all contained a considerable number of other products additional to acetone and the cyclobutanol (see Fig. 3 and Tables I-V). A number of these products were common to many of the photoreaction mixtures.

2-Pentanone formed the greatest number of additional products and so its reaction mixtures were the most intensively studied. This was done by comparing separate and mixed injections of the photoreaction mixtures and authentic samples of suspected products, on both columns used (FFAP and Apiezon L).

2-Propanol and the three reduced ketones (2-pentanol, 4-methyl-2-pentanol and 2-hexanol) were identified by this method. However, a number of other compounds, even those with a remote possibility of being products (methanol, ethanol, 1-propanol, 1-butanol, 2-butanol, 1-pentanol, propanal, butanal, methyl acetate, 2,3-butandione, tetrahydrofuran, cyclopentanone, cyclopentane, hexane, heptane), were tested without success. Low boiling components of Type I (e.g. carbon monoxide, methane, propane) and Type II (ethene) reactions, which have been reported by many authors [7,32,109], were not identified but were assigned to a large peak of very short retention time which appeared on all chromatograms (see Fig. 3, page 65).

The only other product to be tentatively identified was ethanal. This was tentatively identified in some reaction mixtures from all three ketones. It was, however, only formed in significant amounts when ethanol (an amount equal to ± 50% of the acetone formed) and 1,2-ethandiol (± 110% of the acetone) were the solvents. In dodecane, 1-heptanol, 1-octanol, 1-decanol, 1-dodecanol and 1,2-propandiol, there are indications of traces of ethanal in all ketones used. All secondary alcohol solvents failed to give any indication of formation of ethanal.

Later work has also shown the presence of ketals in the photolysates from some alcohol solvents (see Experimental, section G2).

G. Other Experiments

1. Comparison of Photolyses of Air- and Nitrogen-saturated Solutions

Two experiments (using 2-pentanone in hexane and ethanol) were performed to see if removal of the dissolved oxygen by displacement with nitrogen produced a difference in the results. Nitrogen gas was passed through 50 ml of the solvents for ten minutes. Solutions of 2-pentanone in these solvents were then quickly made up as usual. Control solutions of 2-pentanone in hexane and ethanol which had not been flushed with nitrogen were irradiated and analysed at the same time. The results for all four photolyses are presented in Table VIII (page 75). In hexane, the yield of a number of minor products appeared to be enhanced when nitrogen was present instead of air.

2. Experiments on Ketal Formation and the Gas Chromatographic Identification of Ketals

0,23M Solutions of (i) acetone and (ii) 2-pentanone in 1,2-ethandiol were allowed to stand for a few days. No ketal formation could be detected on the g.c. Two fresh 0,23M solutions were then made-up and irradiated*. In the analysis of the products of these irradiations, four columns were used. The FFAP and Apiezon columns previously described were used and, in addition, two further six foot stainless steal columns (one 1/4 inch diameter with Hyprose SP80

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* This investigation was undertaken after the original work had been completed and the photolytic conditions of the previous work could not be precisely reproduced since a different lamp had to be used. However, since in all other ways the irradiations were performed in a manner identical to the earlier ones, it is unlikely that any significant differences resulted.

Table VIII 2-Pentanone: Average peak heights (cm) of components of irradiated solutions (air- and nitrogen-saturated) as determined on FFAP column

| Solvent | Acetone | 2-Propanol | 2-Pentanone | 2-Pentanol | 1-Methyl-cyclo-butanol | Unknown (retention time 9,8min) | Total peak heights |
|---|---|---|---|---|---|---|---|
| Hexane (air-saturated) | 4,3 | 0,5 [a] | 10,0 | 2,3 | 4,1 | 1,8 | 23,0 |
| (nitrogen-saturated) | 5,2 [a] | 0,8 | 7,3 | 2,3 | 5,0 | 3,0 | 23,6 |
| Ethanol (air-saturated) | 6,9 | b | c | 8,8 | 5,5 | 5.5 | 26,7 |
| (nitrogen-saturated) | 5,9 | b | c | 9,8 | 6,2 | 5,8 | 27,7 |

a) approximate measurement

b) peak height was not measured as peak was not sharp enough

c) not measurable as peak was obscured by solvent

(11% on Supelcoport), the other 1/8 diameter with GESE 52 (5% on chromsorb W)), were employed.

*In the irradiated solution of acetone in* 1,2-ethandiol, the corresponding ketal was tentatively identified by virtue of the resolution obtained on the Apiezon L column. It was estimated to be about 10% of the original acetone. On the other three columns it could not be clearly resolved from a large unidentified product peak. In the irradiated 2-pentanone solution, the presence of the corresponding ketal (about 5-10% of the 2-pentanone) was tentatively identified on the grounds of the separation obtained on the Hyprose column. No clear information was obtained using the other columns. On the FFAP and GESE 52 columns the ketal peak corresponded in retention time to the peak identified as 1-methylcyclobutanol, while on the Apiezon L column it corresponded in retention time to the solvent. The presence of *2,2-dimethyl-1,3-dioxolane in the irradiated* 2-pentanone solution could not be clearly established since it was not clearly resolved on any of the columns used. On the Apiezon L column its retention time corresponded to that of 2-pentanone.

In a limited investigation of possible ketal formation during irradiation of ketones in monohydric alcohols, the solvent methanol was chosen for study. The ketal from acetone (2,2-dimethoxypropane) *had the same retention time as acetone on the FFAP column* and as methanol on the Apiezon L column. Hence its presence in the irradiated methanol solutions could not be established. However, the ketal from 2-pentanone (2,2-dimethoxypentane) was partly resolved from 2-pentanone on the FFAP column under the normal operating conditions (see Experimental, section C, and a peak corresponding to this compound was indeed observable on the side of the 2-pentanone peak in the

gas chromatograms previously obtained from irradiated solutions of 2-pentanone in methanol.

3. Irradiation Acetone in Various Solvents

As it seemed possible that the 2-propanol was derived from photoreduction of acetone, first formed by Type II elimination from the original ketone, a trial photolysis of acetone was performed. Acetone (0,2M) was irradiated in hexane under the same conditions as for the ketones studied. After the 20 hours irradiation more than 80% of the acetone had reacted and 2-propanol (50-60%) and other unidentified products were produced. Similar results were obtained on irradiation of solutions of acetone in 1,2-ethandiol and 1-decanol. The amount of 2-propanol formed in 1-decanol was approximately 80% of the total observable photoproducts.

# DISCUSSION

The principal aim of this discussion is to interpret the comparative behaviour of the three ketones in the range of solvents studied. However, as a preliminary it is necessary to discuss the photoketalization reaction which has been found to occur in alcohol solvents. The explanation of the chosen method of treatment and presentation of results for discussion, will show the consequences for the interpretation of the results of this photoketalization and the need to discuss this first. Thus this discussion is divided into four main sections as follows:

A The photoketalization reaction

B Method of treatment of results

C Comparison of the behaviour of the different ketones

D Comparison of the effects of the different solvents

## A. The Photoketalization Reaction

During the analysis of the data reported in this work anomalously low acetone yields were revealed in the case of the photolysis of all three ketones in 1,2-ethandiol solution. One possible explanation of this, which subsequent experiments proved, was that a ketalization reaction occurred in this solvent.

Since no acid or base catalysis should be operative under the photolysis conditions, a search of the literature was made for reports of uncatalysed ketal formation. Only two relevant reports were found. In one it was suggested that reaction occurs between methanol and

cyclohexanone to form the ketal in the absence of acid catalyst in the course of a few hours at room temperature or a few minutes at 100°C [137]. In the other a transketalization between chloroacetal and 1,2,3-propantriol was reported to occur on heating them together at 115°C for a short period [138]. This literature search also revealed that u.v. light-catalysed ketal formation is not unknown [139]. Nevertheless it does not appear to have been considered by the vast majority of workers in the field of ketone photochemistry, when analysing their results. The most recent report is that of Dirania and Hill on the photoketalization of α-aryloxyacetones [139]. These authors obtained ketals from irradiations in methanol, ethanol and benzyl alcohol but not in a 1,2-ethandiol/dioxan mixture or in secondary alcohols (2-propanol and cyclohexanol). They also suggest that the ether oxygen present in these ketones plays an important role in this photoketalization since they found that ketones which lack the ether function, but are otherwise analogous, did not undergo the reaction.

In view of the paucity and somewhat conflicting nature of literature reports, a direct test was made to see if an uncatalysed thermal ketalization reaction could occur between simple ketones and 1,2-ethandiol. It was found that solutions of 2-pentanone and acetone in 1,2-ethandiol showed no ketal formation after standing for several days at room temperature. In order to test the photoketalization hypothesis, samples of the 1,2-ethandiol ketals of acetone (2,2-dimethyl-1,3-dioxolane) and 2-pentanone (2-methyl-2-propyl-1,3-dioxolane) were prepared *. By g.c. peak matching the former was identified as a product from the irradiation of acetone, 4-methyl-2-pentanone and 2-hexanone

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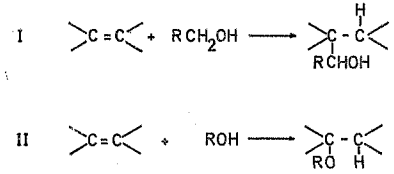
* These were kindly supplied by Mr J. Michael - see Experimental, section A2(c).

in 1,2-ethandiol. Furthermore, the 2-pentanone ketal was tentatively identified in the irradiated reaction mixtures of 2-pentanone in 1,2-ethandiol. Using the g.c. conditions which were employed in the analysis of earlier photolysates, it is however not separated from 1-methylcyclobutanol.

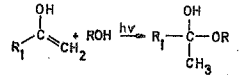
Subsequent experiments in this laboratory have shown that irradiation of 2-pentanone in simple primary alcohol solvents (methanol and 1-octanol) also gives rise to varying amounts of ketals [140]. It would thus appear that, contrary to the suggestion of Dirania and Hill [139], this is a photoreaction of some generality. Thus the gas chromatograms obtained earlier in this work were inspected and found, in the case of several alcohol solvents, to exhibit peaks which could be reasonably assigned to the ketals of acetone and the relevant ketone. It is not easy to estimate a general figure for the extent of ketal formation in the irradiations performed in this work, but it certainly does not exceed 20% of the reaction. Judging from subsequent results obtained in these laboratories, it is probably significantly less for irradiations done in longer chain alcohols [140].

Since the information on this reaction is so limited it is not possible to infer much about its mechanism. Photo-addition of alcohols to C=C bonds is well documented [141] and both radical and polar paths have been postulated for these. The former is postulated for addition mode I and the latter for addition mode II.



The ketalization must be analogous to the polar addition mode II as it is difficult to see how a radical pathway could lead to ketal formation. Although it seems attractive to invoke the radical-like properties of ketone excited states, such a possibility would appear reasonably, only to lead to an addition of mode I-type. A polar addition to the excited carbonyl group of the ketone obviously accounts for the ketalization in a general way, but the addition mode II seems inconsistent with the expected polarity of the ketone excited state (see Introduction, section C1). Another possibility is that addition actually occurs to an enol tautomer (possibly a photoenol) as in Scheme XVII.

Scheme XVII



The involvement of a photoenol is an appealing possibility for the acetone ketalization, since the acetone is initially eliminated as the photoenol. However, no photoenol of the starting ketone has ever been identified in photolysates, although such an intermediate has been postulated to occur in the photolysis of 2,3-butandione [142]. They have also been postulated as intermediates in photoisomerizations [53,143] and have been isolated as products in the photolyses of a number of 1-phenylalkan-1,2-diones [72,73] and o-benzylbenzophenone [108]. Thus it could be claimed that photoenols are formed by simple ketones as well, but that they form in low yields and/or rapidly return to the starting ketone. Although this is a possibility, there are further difficulties with the postulate of an intermediate photoenol on the path to photoketalization. Presuming that addition of alcohol to the photoenol has to be photochemically initiated, the difficulty arises that the photoenol may have an excitation energy greater than that supplied by the wavelength of radiation used [141]. It is, of course, possible that the ketone could photosensitise the reaction of the enol. The involvement of a photoenol perhaps looks rather unlikely in these circumstances, but it cannot be ruled out altogether.

In a recent article Reardon and Kropp have suggested that a radical cation mechanism of addition to C=C bonds can occur under certain *irradiation conditions* [144] *. *They reported addition of alcohol* solvent molecules across C=C bonds using radiation of comparatively short wavelength (in quartz vessels). From the type of products obtained, they suggest the pathway in scheme XVIII for the alcohol addition.

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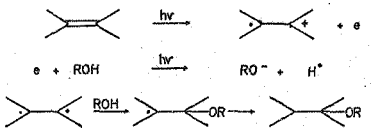
* The radical cation may in fact be the singlet excited state of the olefin, which is considered to be a Rydberg-like state.

Scheme XVIII



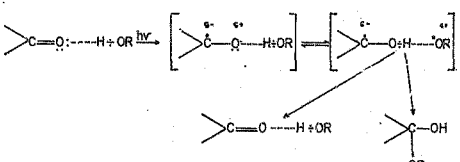

It is uncertain whether the longer wavelength radiation used in the present work would be sufficiently energetic to cause a similar electron ejection from the ketone but it seems unlikely. In any case, ejection of a non-bonding electron from the oxygen would make it positively charged and this is not an attractive intermediate from which to visualise formation of a ketal.

It would thus appear that no explanation based on analogy with previous observations and hypotheses in the literature is entirely satisfactory. Therefore, a further hypothesis is suggested. The oxygen of the carbonyl group is undoubtedly hydrogen-bonded to the hydroxyl group of the alcohol molecule. The hydrogen will not be symmetrically located between the two oxygen atoms involved but will spend time at a site near to one or the other oxygen atom. Probably it will spend more time near the alcohol oxygen than the carbonyl oxygen since this position will give rise to less charge separation and will probably be of lower energy. On $n\pi^*$ excitation of the carbonyl group, the carbonyl oxygen becomes electron deficient, and the site for the hydrogen atom near to this carbonyl oxygen atom,

may now become of lower or comparable energy to the site near to the alcohol oxygen atom. Movement of the hydrogen atom to this site would give a dipolar complex which could reasonably collapse back to the starting materials or to the addition product.

The above description is rendered in Scheme XIX using a partial dipole valence-bond representation of the carbonyl excited state for convenience.

Scheme XIX



It is suggested that the abstraction of hydrogen from the hydroxyl group of the alcohol, is competitive with the normal α-hydrogen abstraction only in the special circumstances of the pre-oriented, and possibly excessively-energised, hydrogen-bonded excited state. A relaxed equilibrated excited state evidently behaves very similarly to free alkoxy radicals (see introduction, section D 1(a)). There is a weak and not entirely satisfactory analogy to the present hypothesis in the hypothesis advanced by Turro and coworkers in explanation of the quenching of 2,3-butandione luminescence by phenols [145,146]. Hydrogen transfer from the phenol was proposed as the mechanism of quenching, and its efficiency was found to be better the greater the electron releasing power of the phenol substituent. As hydrogen abstraction from phenols by radicals occurs preferentially from the hydroxyl group

anyway, it must be admitted that the analogy is not particularly good.

B. *Treatment of Results*

1. Form of Presentation of Results and Some Factors Affecting Their Reliability

The peak heights recorded in the Experimental, section D, were reduced to percentages of the sums of the peak heights of the identified components. The reason for quoting the proportion of each component as a percentage of all identified components in each solvent, was to eliminate certain experimental variables. The principal aim was to compensate in a simple way for variations in g.c. analysis conditions (injection size, column performance, programming rate, flow rate, detector conditions). In addition variance in the exact initial concentration of the photolysis solutions, would be compensated for. Variations in the u.v. lamp output (intensity) would not be compensated for by this procedure of course, but it was considered that this would not be too serious. In the event, photolyses performed at different times with the same reaction mixtures gave results in satisfactory agreement. In six cases significant differences were observed and in these cases both sets of results are recorded (see Experimental, section D). Even in these cases the qualitative conclusions are not altered whichever set of results is chosen.

This method of handling the experimental data has potential drawbacks which could lead to erroneous conclusions. The most serious potential problem is that there may be other photoproducts which are not eluted from the g.c. columns within the time interval that the g.c. recorder is operating. These are then omitted from the summation of all the peak heights for that photoreaction, thus giving

the recorded components, percentages greater than the true values. This possibility is not regarded as too serious an objection as (i) from reviews of the field of ketone photochemistry [22,32,41,109] it can be seen that all the commonly documented photoproducts have been taken into account, and (ii) if there are products unaccounted for, the variation in their yields from ketone to ketone and solvent to solvent should result in only minor pertubations in the relative yields of the identified components. Although these arguments can be considered reasonable, the possibility of error arising in this way must be recognised.

There are two more specific points to be noted in connection with the results. The first point is that the 4-methyl-2-pentanone used, contained an impurity which had a g.c. retention time corresponding to that of 4-methyl-2-pentanol under all conditions tested. Presumably, the impurity was this alcohol. As a result no reliable estimate of the yield of this product from the photoreactions of 4-methyl-2-pentanone could be obtained. The contribution of this product to the total composition was therefore omitted. The percentages derived for all the other components are therefore all higher than the true figures by a small amount. The discrepancy must, however, be quite small and seems unlikely to have any disturbing effect on qualitative comparisons of behaviour.

The other point relates to the proportion of the acetone produced from all three ketones. As will be mentioned later, the formation of 2-propanol is one of the secondary reactions of acetone that has been identified. Thus the peak of the 2-propanol should be added to that of the acetone in order to get a proper estimate of the proportion of Type II elimination. However, the 2-propanol almost invariably gives

rise to a small g.c. peak. In some cases it was an ill-defined peak and could not be satisfactorily measured. It was therefore felt that to omit inclusion of this small peak (2-propanol) in all cases would be the best procedure and would have no great effect on the respective acetone yields for comparative purposes.

In some solverts complete product analysis could not be performed for one reason or another (e.g. overlap of solvent peak with product peak under the chosen g.c. operating conditions). In these circumstances the general procedure for presentation of data could not be followed and limited conclusions are drawn therefore from simple comparisons of peak heights for certain compounds of interest.

The results from the pentadiene-quenched and short-term irradiations are also presented in a limited form. The peak heights of two products of interest (acetone and substituted cyclobutanol) are given only as, with the low degree of conversion characteristic of these experiments, the proportion of residual ketone could not be reliably measured.

The presence of dissolved air in the solutions did not appear to affect the results, since experiments performed with nitrogen-saturated and air-saturated solutions gave very similar results (Table IX - page 88). This is in line with the findings of Guillet and coworkers who found no change in the quantum yields of reaction when a series of 2-alkanones were photolysed under nitrogen instead of in air [11]. Thus no variation of results due to variable proportions of dissolved air should occur.

2. Effect of the Photoketalization Reaction on the Analysis of the Results

The discovery of the generality of the photoketalization reaction was made at a late stage in the present work. Thus whilst it was of

Table IX 2-Pentanone: Analysis of photoreaction mixtures from irradiations in air and under nitrogen[a]

| Solvent | Percentage of total components measured | | | | | | Ac/cb |
|---|---|---|---|---|---|---|---|
| | Acetone (Ac) | 2-Propanol | 2-Pentanone | 2-Pentanol | 1-Methyl-cyclobutanol (cb) | Unknown (retention time 9,8min) | |
| Hexane (air-saturated) | 19 | 2 | 43 | 10 | 18 | 8 | 1,0 |
| (nitrogen-saturated) | 22 | 3 | 31 | 10 | 21 | 13 | 1,0 |
| Ethanol (air-saturated) | 26 | - | - | 33 | 21 | 21 | 1,3 |
| (nitrogen-saturated) | 21 | - | - | 35 | 22 | 21 | 1,0 |

a) results derived from data in Table VIII, and quoted as 100 x individual/Total peak heights

considerable interest, it was not possible to thoroughly explore its significance in regard to the present work and to make precise estimates and allowances for ketal formation by repeating all of the analyses under modified conditions. As careful an assessment as possible was therefore made of its expected impact on the analysis and interpretation of the results.

(a) Comparison of the photoreactions of the various ketones

Only extremely limited data bearing on this point is to hand, but there are no grounds for suggesting that significant differences exist in the extent of ketal formation undergone by the three ketones on irradiation in a particular alcohol. Hence comparisons of the results obtained for the three ketones which involve estimates of the residual ketone and/or acetone should be valid.

(b) Comparison of the photoreactions in the various solvents

The problem here is potentially far more serious since the extent of ketal formation is apparently influenced quite significantly by the nature of the alcoholic solvent. Hence comparisons involving the amount of residual ketone and/or the product acetone must be treated with care. As will be discussed later in the relevant sections, however, allowance for the influence of ketal formation would in fact serve only to accentuate the qualitative trends which are observed in the present results.

C. Comparison of the Behaviour of the Different Ketones

1. Extent of Reaction and Quantum Yield

The proportion of residual ketone may be taken as a measure of the extent and quantum yield of total reaction assuming comparable photolysis conditions in all cases. Any ketal formation by the ketone should have little effect due to the approximately equal amounts of

Table X 2-Pentanone: Percentages of components present in photoreaction mixtures in various solvents [a]

| Solvent | Acetone (Ac) | 2-Propanol | 2-Pentanone | 2-Pentanol | 1-Methyl-cyclobutanol (cb) | Unknown (retention time 9,8min) | Ac + cb | Ac/cb |
|---|---|---|---|---|---|---|---|---|
| Hydrocarbons | | | | | | | | |
| Hexane | 18 | 6 | 44 | 7 | 17 | 8 | 35 | 1,1 |
| | 21 | 4 | 45 | - | 22 | 8 | 43 | 0,93 |
| Dodecane | 19 | 3 | 56 | 8 | 15 | - | 33 | 1,2 |
| Hexadecane | 15 | 5 | 46 | 9 | 14 | 10 | 30 | 1,0 |
| "Nujol" | 12 | - | 53 | 12 | 11 | 12 | 23 | 1,0 |
| Average | 17 | | 49 | | 16 | | 33 | 1,0 |
| Alcohols | | | | | | | | |
| Methanol | 37 | - | 38 | 2 | 22 | 1 | 59 | 1,7 |
| Ethanol | - | - | - | - | - | - | - | 1,2 |
| 1-Heptanol | 19 | 4 | 41 | 19 | 17 | - | 36 | 1,1 |
| 2-Octanol | 21 | 5 | 43 | 16 | 8 | 8 | 29 | 2,6 |
| 1-Decanol | 19 | - | 45 | 13 | 11 | 11 | 30 | 1,6 |
| Average | 24 | | 42 | | 15 | | 39 | 1,6 |
| 1,2-Ethandiol | 9 | - | 36 | 20 | 19 | 16 | 28 | 0,49 |
| 1,2-Propandiol | 15 | - | 56 | 11 | 9 | 9 | 24 | 1,8 |

a) results derived from data in Table I, and quoted as 100 x Individual/Total peak heights

Table XI 4-Methyl-2-pentanone: Percentages of components present in photoreaction mixtures in various solvents [a]

| Solvent | Acetone (Ac) | 2-Propanol | 4-Methyl-2-pentenone | 1,3-Dimethyl-cyclobutanol (cb) | Ac + cb | Ac/cb |
|---|---|---|---|---|---|---|
| Hydrocarbons | | | | | | |
| Hexane | 38 | - | 50 | 12 | 50 | 3,0 |
| | 30 | - | 61 | 9 | 39 | 3,5 |
| Dodecane | 27 | 3 | 62 | 7 | 34 | 3,7 |
| Hexadecane | 25 | 3 | 66 | 6 | 31 | 4,1 |
| "Nujol" | 20 | 4 | 65 | 10 | 30 | 1,9 |
| Average | 28 | | 61 | 9 | 37 | 3,2 |
| Alcohols | | | | | | |
| Methanol | 43 | - | 50 | 7 | 50 | 6,4 |
| | 44 | - | 49 | 6 | 51 | 6,9 |
| Ethanol | 37 | - | 35 | 28 | 65 | 1,3 |
| | 42 | 3 | 42 | 13 | 54 | 3,3 |
| 1-Heptanol | 39 | 7 | 33 | 21 | 61 | 1,8 |
| | 33 | 3 | 52 | 12 | 45 | 2,8 |
| 2-Octanol | 31 | 3 | 62 | 4 | 35 | 7,3 |
| 1-Decanol | 37 | 4 | 47 | 11 | 48 | 3,2 |
| Average | 38 | | 46 | 13 | 51 | 4,1 |
| 1,2-Ethandiol [b] | 10 | - | 44 | c | 10 | d |
| 1,2-Propandiol | 32 | 3 | 55 | 10 | 42 | 3,2 |

a) results derived from data in Table II, and quoted as 100 x individual/Total peak heights
b) there is a 45% contribution to the total for suspected ketal peaks c) small d) large

Table XII 2-Hexanone: Percentage of components present in photoreaction mixtures in various solvents [a]

| Solvent | Acetone (Ac) | 2-Propanol | 2-Hexanone | 1,2-Dimethylcyclobutanol (cb) | | | Ac + cb | Ac/cb |
|---|---|---|---|---|---|---|---|---|
| | | | | trans | cis | total | | |
| *Hydrocarbons* | | | | | | | | |
| Hexane | 17 | - | 68 | 8 | 8 | 15 | 32 | 1,1 |
| Dodecane | 16 | 1 | 75 | 8 | - | - | - | - |
| Hexadecane | 17 | 1 | 69 | 7 | 6 | 13 | 30 | 1,3 |
| "Nujol" | 13 | 1 | 71 | 7 | 7 | 14 | 27 | 0,96 |
| Average | 16 | | 71 | | | 14 | 30 | 1,1 |
| *Alcohols* | | | | | | | | |
| Methanol | 21 | - | 66 | 8 | 6 | 14 | 34 | 1,5 |
| Ethanol | 21 | - | 64 | 8 | 7 | 15 | 36 | 1,5 |
| 1-Heptanol | 18 | 2 | 65 | 8 | 6 | 14 | 33 | 1,3 |
| 2-Octanol | 18 | 1 | 72 | 4 | 4 | 9 | 26 | 2,1 |
| 1-Decanol | 18 | 2 | 68 | 6 | 6 | 12 | 30 | 1,8 |
| Average | 19 | | 67 | | | 13 | 32 | 1,8 |
| 1,2-Ethandiol [b] | 7 | 1 | 63 | 9 | 7 | 16 | 23 | 0,44 |
| 1,2-Propandiol | 12 | 2 | 77 | 4 | 4 | 9 | 21 | 1,4 |

a) results derived from data in Table IV, and quoted as 100 x individual/Total peak heights

b) there is a 13% contribution to the total for suspected ketal peaks

ketal formation expected for all three ketones. The results in Tables X to XII (pages 90 to 92) indicate the following order of photoreactivity in all solvents studied *.

2-pentanone > 4-methyl-2-pentanone > 2-hexanone

This order is in accordance with expectations based on the available literature reports. For example, some total quantum yields for 2-pentanone and 2-hexanone photolyses that have been reported are in Table XIII.

Table XIII Literature values of total quantum yields for 2-pentanone and 2-hexanone

| Ketone | Total quantum yield of reaction | Solvent | Reference |
|---|---|---|---|
| 2-Pentanone | 0,39 | hexane | 28 |
| 2-Pentanone | 0,42 | hexane | 10 |
| 2-Hexanone | 0,33 | hexane | 28 |
| 2-Hexanone | 0,33 | pentane | 17 |

The nature and number of the available γ-hydrogen atoms probably account for this order. Thus the secondary nature of the γ-hydrogens in 2-hexanone will lead to more singlet participation (see Introduction, section C3(b)), and thus a lower quantum yield of reaction than 2-pentanone which has only primary γ-hydrogen atoms. Similarly, the greater number of primary γ-hydrogens of 4-methyl-2-pentanone as compared to 2-pentanone will promote γ-hydrogen abstraction, thus giving rise to greater singlet participation and similar consequences.

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* A similar sequence is indicated by the sum of the yields of acetone and cyclobutanol.

It is evident from the present results that the various solvent effects reported in the literature and observed in this work do not seriously perturb the intrinsic differences between the three ketones. Thus support is given to the current literature interpretations of structural effects on the quantum yield of alkanone photolysis.

2. Singlet and Triplet State Contributions

A few photo-quenching experiments were performed using the triplet quencher cis-1,3-pentadiene. Following the report of excess pentadiene causing some quenching of the singlet state [36] and the tendency of recent researchers [28,48] to use quencher concentrations comparable to the ketone concentration, a quencher concentration of 0,15M (versus 0,23M for the ketone) was used. Wagner and Hammond found that a Stern-Volmer plot of unquenched/quenched quantum yields versus quencher (1,3-pentadiene) concentration for 2-pentanone in hexane, only reached a limiting value of about 8,3 at 8M quencher [10]. For 0,15M quencher the ratio of unquenched to quenched quantum yields was only 3,5. Similarly with 2-hexanone the relevant ratios were 2,4 at 8M quencher and 1,6 at 0,15M quencher concentration. Thus even though triplet quenching was probably incomplete in the present experiments, reliable qualitative comparisons of the relative proportions of triplet contribution to the total photoreaction of the different ketones should be possible.

The limited results do permit approximate deductions concerning the relative contributions of the singlet and triplet states in the photoreactions of 2-pentanone and 2-hexanone (the peaks assigned to the cyclobutanols could not be clearly observed in the quenching experiments of 4-methyl-2-pentanone). From the results presented in Table VI it can be seen that the product yields in the presence of quencher are far lower than in the absence of quencher. It is also noticeable that

the cyclobutanol yields are particularly greatly diminished and, as shown in the table below, this gives rise to greater acetone/cyclobutanol ratios than found in the absence of quencher. This is in line with literature reports that the cyclobutanol is predominantly a triplet state product whilst acetone is formed from both states.

Table XIV Acetone/cyclobutanol ratios of quenched, unquenched and short-term photolyses of 2-pentanone and 2-hexanone [a]

| Solvent | Ketone [b] | Quenched | Unquenched | Short-term |
|---|---|---|---|---|
| "Nujol" | 2P | 5,5 | 1,0 | - |
| | 2H | 2,3 | 0,96 | - |
| Methanol | 2P | 7,3 | 1,7 | 1,7 |
| | 2H | 3,8 | 2,1 [c] | - |
| 2-Octanol | 2P | 11,8 | 2,6 | 2,9 |
| | 2H | 4,3 | 2,1 | - |
| Hexadecane | 2P | 6,7 | 1,0 | 1,4 |
| Ethanol | 2P | 3,0 | 1,2 | 1,8 |
| Cyclohexanol | 2P | 4,1 | 2,2 | 1,3 [d] |
| Hexane | 2P | - | 1,0 [c] | 1,6 [d] |
| 1-Heptanol | 2P | - | 1,1 | 1,2 |
| 1-Decanol | 2P | - | 1,6 | 3,3 |
| 1,2-Propandiol | 2P | - | 1,8 | 1,3 |

a) results derived from data in Tables VI and VII

b) 2P = 2-pentanone, 2H = 2-hexanone

c) average from both sets of results in Tables I to IV

d) approximate

In the case of 2-pentanone the acetone/cyclobutanol ratio is about five-fold greater in the quenched as compared to the unquenched photolyses, whilst in the case of 2-hexanone there is roughly a two-fold difference (Table XIV). On the basis of this admittedly limited data, the order of decreasing triplet contribution is:

2-pentanone > 2-hexanone

As noted in the previous section this is in accord with literature reports regarding these two ketones (see Table XV below).

Table XV Literature values of singlet and triplet quantum yields of reaction for 2-pentanone and 2-hexanone

| | Quantum yield of reaction | | | |
|---|---|---|---|---|
| Ketone | *Singlet* | *Triplet* | Solvent | Reference |
| 2-Pentanone | 0,03 | 0,36 | hexane | 28 |
| 2-Pentanone | 0,05 | 0,38 | hexane | 10 |
| 2-Hexanone | 0,10 | 0,23 | hexane | 28 |
| 2-Hexanone | 0,11 | 0,23 | pentane | 17 |

Again it may be noted that the present results establish that the proportion of singlet and triplet state reaction is a property at least primarily characteristic of a given ketone, and that it is little affected by the nature of the solvent.

A few short-term, unquenched irradiations were performed to establish that the differences between the quenched and unquenched acetone/cyclobutanol ratios were not due to the much smaller extent of reaction in the quenched photoreaction experiments. In Table XIV, the acetone/cyclobutanol ratios for the unquenched short-term and long-term irradiations are compared. The ratios from the short-term

irradiations are slightly higher than those from the unquenched long-term irradiations but it can be seen that they differ markedly from the ratios from the long-term quenched irradiations. It thus appears that whilst there are small changes in the acetone/cyclobutanol ratio with the extent of conversion, this is not an explanation of the results obtained in the long-term quenched irradiations.

3. Acetone and Cyclobutanol Yields

*Irrespective of the variation in the relative yields of the* products due to solvent variance, there are consistent differences between 2-pentanone and 2-hexanone on the one hand and 4-methyl-2-pentanone on the other (see Tables X-XII). The order of acetone yields amongst the three ketones in both hydrocarbon and alcohol media is: *

4-methyl-2-pentanone > 2-pentanone > 2-hexanone

whilst the order of cyclobutanol yields is:

2-pentanone > 2-hexanone > 4-methyl-2-pentanone

An explanation for these two different orders, may be given in terms of the nature and number of the γ-hydrogen atoms, and steric effects on the intermediate 1,4-biradical behaviour.

(i) The secondary nature of the γ-hydrogens of 2-hexanone leads to a greater singlet contribution relative to 2-pentanone (with primary γ-hydrogens). Since there is more efficient reaction from the triplet state (especially in regard to cyclobutanol formation [27,28,49]) it is not surprising that

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* The order for the elimination in the gas phase is 2-hexanone > 4-methyl-2-pentanone > 2-pentanone [7,69,147]. This change is presumably connected with the greatly increased Type I reaction quantum yield in the gas phase.

2-pentanone gives greater acetone and cyclobutanol yields than 2-hexanone.

(ii) The increased number of primary γ-hydrogens in 4-methyl-2-pentanone as compared to 2-pentanone, should give rise to a greater proportion of singlet reaction in the former case. In addition, on account of the differing steric requirements of the biradical conformations that lead to elimination and cyclization (see introduction, section D2(c)), β-substituents lead to a preference for elimination over cyclization [94]. This effect has been reported for aryl alkyl ketones but presumably is also operative for dialkyl ketones. Hence 4-methyl-2-pentanone could indeed give the highest acetone and lowest cyclobutarol yields of the three ketones.

The relative magnitudes of the acetone/cyclobutanol ratio for these three ketones are therefore more or less as expected (4-methyl-2-pentanone > 2-hexanone > 2-pentanone). However, they are smaller than those reported in the literature for 2-pentanone and 2-hexanone (Table XVI).

Table XVI Acetone/cyclobutanol ratios for 2-pentanone and 2-hexanone

| Ketone | Present work (average) | Literature |
|---|---|---|
| 2-Pentanone | 1,3 | 2,2 (neat - ref. 14) |
| 2-Hexanone | 1,5 | 2,3 (in pentane - ref. 17) |

The extent of conversion may be a factor here because, as noted before, the acetone/cyclobutanol ratios for the short-term irradiations are on the average higher than those obtained for the long-term irradiations. Secondary reactions of the acetone seem a likely explanation of these differences and though 2-propanol was accounted for (see next section)

other possible photoproducts from acetone were not. These other products could derive, for example, from coupling of the 2-hydroxy-2-propyl radical with any of the other radicals in the reaction system [148] as well as the photoketalization already discussed. The low acetone/cyclobutanol ratios found in the present experiments are thus easily explained, although it is not possible to confirm the explanation without further experiments. It seems unlikely that these secondary reactions would affect any qualitative comparisons however.

4. Photoreduction

Photoreduction of the parent ketone and, to a small extent, the eliminated acetone, was observed in all experiments. It was pointed out in the introduction that photoreduction is a triplet state process. However, in the quenching experiments it was seen that some reduction of both the ketone and the acetone still occurred in all cases. Most likely this is from some unquenched triplet reaction (see Discussion, *section C2), although photoreduction from the singlet* state is a possibility.

The observed percentages of the photoreduction product from two of the ketones are summarised in Table XVII (the 4-methyl-2-pentanol from 4-methyl-2-pentanone could not be determined (see Discussion, section B(1)), and are seen to fall in the sequence:

2-pentanone > 2-hexanone

i.e. the same order as for total reaction and presumably that of decreasing triplet contribution.

Table XVII Yield of reduced ketone as a percentage of the products in photoreaction mixtures

| Solvent | 2-Pentanol [a] | 2-Hexanol [b] |
|---|---|---|
| Hexane | 12 | 4 |
| Dodecane | 16 | 4 |
| Hexadecane | 17 | 4 |
| "Nujol" | 26 | 6 |
| Methanol | 4 | 1 |
| Ethanol | 35 | 5 |
| 2-Octanol | 28 | 0,4 |
| 1-Decanol | 24 | 4 |

a) from 2-pentanone; derived from data in Table I

b) fror 2-hexanone; from Table IV

Secondary photoreduction of the eliminated ketone (in the present experiments, acetone giving 2-propanol) is to be expected and indeed has been reported in the literature [117]. In the short-term irradiations the amount of 2-propanol produced was very small as would be expected if it is a secondary reaction product. Three experiments in which acetone was irradiated in hexane, 1,2-ethandiol and 1-decanol showed the feasibility of this interpretation. At a high conversion of acetone, 2-propanol and a number of further (unknown) products were seen on gas chromatographic separation of the mixture. However, the 2-propanol yield from these irradiations was always at least equal to the total yields of the unknown products. Some of these unknown products were also detectable in the g.c. traces of a few photolysates previously obtained. Presumably they correspond to

combination of the 2-hydroxy-2 propyl radical with solvent-derived radicals.

The yield of 2-propanol in the photolysates from 2-pentanone, 4-methyl-2-pentanone and 2-hexanone was always small and its proportion varied little from one case to another.

D. Comparison of the Effects of the Different Solvents

1. Polarity and Chemical Nature of the Solvent

(a) Extent of photoreaction

Greater total reaction quantum yields are expected in more polar solvents, although the effects reported are not large for alkanones (see Introduction, section E2). According to Wagner and coworkers *the effect may be related to the basicity of the solvent* [117], rather than its polarity as measured by the electronegativity or dipole moment. A factor complicating the comparisons is the variation in the relation between quantum yield and irradiation time in different solvents. For example, in the case of valerophenone, the quantum yield diminishes at conversions greater than 20% when the reaction is carried out in 1-propanol but in benzene solution it only diminished at conversions of greater than 75% [117]. In the present work, conversions of around 60% were achieved in the irradiation time used and this would suggest that there may be a larger decrease in quantum yields for the irradiations carried out in alcohol solvents as compared to hydrocarbon solvents. However, comparison of the extent of reaction as measured in the present work should be only moderately influenced by such quantum yield variations.

Taking the remaining ketone as a measure of the total extent of reaction, it can be seen from the data in Table XVIII below that the extents of reaction are greater in the alcohol solvents for all three ketones. The same effect is shown by the sums of the acetone and

cyclobutanol yields, those being the product yields of principal interest.

Table XVIII Average results for the extent of photoreaction of the three ketones [a] in different solvent types

| Solvent type | Percent residual ketone | | | Percentage acetone + cyclobutanol | | |
|---|---|---|---|---|---|---|
| | 2P | 4M2P | 2H | 2P | 4M2P | 2H |
| Hydrocarbons | 49 | 61 | 71 | 33 | 27 | 30 |
| Alcohols | 42 | 46 | 67 | 39 | 51 | 32 |

a) 2P = 2-pentanone, 4M2P = 4-methyl-2-pentanone, 2H = 2-hexanone; data taken from Tables X to XII

A word of caution should be added because the decrease in proportion of residual ketone in the alcohols could be partly due to ketalization of the ketone. However, the average proportion of residual ketone for irradiations in long and short chain alcohols is given and since photoketalization would appear to be much less efficient for long chain alcohols (see Discussion, section A), the perturbing influence of this phenomenon would be attenuated. Furthermore the same trends are indicated by the sum of the acetone and cyclobutanol yields.

As a result of these considerations, it is believed that these qualitative indications of polarity effects are probably reliable.

(b) Acetone and cyclobutanol yields

Several authors have shown that both acetone and cyclobutanol yields should increase with solvent polarity [35,41,49,60,64,96] (see previous section (a)). These authors show (or imply) that this increase in yield with polarity is far greater for the elimination product than

the cyclization product. The data shown in Table XIX below support this belief: indeed with 2-pentanone and 2-hexanone, the average cyclobutanol yields are identical (within experimental error) in hydrocarbon and alcohol media. The effect of solvent polarity might be more pronounced the greater the triplet contribution to product formation, since polarity effects apparently operate only on triplet state reactions. The acetone yield data in Table XIX, are consistent with this, the percentage difference between the yields in alcohols and in hydrocarbons following the trend expected from the above considerations (see also discussion, section C1(a)).

Table XIX Average percentages of acetone and cyclobutanol from the photolyses of the three ketones [a] in solvents of different types

| Solvent type | Percent acetone | | | Percent cyclobutanol | | |
|---|---|---|---|---|---|---|
| | 2P | 4M2P | 2H | 2P | 4M2P | 2H |
| Hydrocarbons | 17 | 28 | 16 | 16 | 9 | 14 |
| Alcohols | 24 | 38 | 19 | 15 | 13 | 13 |
| % Difference | 41% | 36% | 27% | | | |

a) 2P = 2-pentanone, 4M2P = 4-methyl-2-pentanone, 2H = hexanone; data from Tables X to XII

For the alcohol solvents any photoketalization will decrease the acetone yield (unless this ketal elutes with the acetone under the g.c. analysis conditions used). Thus the % difference in Table XIX may be even slightly larger - if the exact amount of photoketalization were known this could be allowed for. Wagner says that he obtained the same quantum yields for Type II reaction of valerophenone in

twelve hydrocarbons and also in five primary alcohol solvents - but the hydrocarbons gave a lower quantum yield than the primary alcohols [35]. In the present work, identical yields of acetone were not obtained from a given ketone in different hydrocarbons or in different primary alcohols (see Tables X to XII). The yields were, however, close enough for average figures to be quoted in Table XIX. This may be a point of difference between aryl alkyl ketones and dialkyl ketones.

Comparison of results in hydrocarbon and alcohol media may also be made through the ratio of yields of acetone to cyclobutanol, although from the literature reports it is evident that this is a less sensitive indicator of effects. This ratio should be greater in the alcohol solvents than in the hydrocarbon solvents and this expectation is confirmed by the data from the present work in Table XX below. Some difference between primary and secondary alcohols is weakly evident but with the limited results available no firm conclusion can be reached on this.

Table XX Acetone/cyclobutanol ratios obtained from photolyses of the three ketones in different solvents [a].

| Solvent | Ketone | | |
|---|---|---|---|
| | 2-Pentanone | 4-Methyl-2-pentanone | 2-Hexanone |
| Hydrocarbons | | | |
| Hexane | 1,0 [b] | 3,3 [b] | 1,1 |
| Dodecane | 1,2 | 3,7 | - |
| Hexadecane | 1,0 | 4,1 | 1,3 |
| "Nujol" | 1,0 | 1,9 | 0,96 |
| Average | 1,0 | 3,2 | 1,1 |
| Primary Alcohols | | | |
| Methanol | 1,7 | 6,7 [b] | 2,1 [b] |
| Ethanol | 1,2 | 2,3 [b] | 1,5 |
| 1-Heptanol | 1,1 | 2,3 [b] | 1,3 |
| 1-Octanol | 1,2 | | |
| 1-Decanol | 1,6 | 3,2 | 1,8 |
| 1-Dodecanol | 1,2 | | |
| Average | 1,3 | 3,6 | 1,7 |
| Secondary alcohols | | | |
| 2-Heptanol | 1,5 | | |
| 2-Octanol | 2,6 | 7,3 | 2,1 |
| 2,6-Dimethyl-4-heptanol | 1,3 | | |
| Cyclohexanol | 2,2 | | |
| Average | 1,9 | (7,3 | 2,1) |
| Miscellaneous | | | |
| 1,2-Ethandiol | 0,49 | c | 0,44 |
| 1,2-Propandiol | 1,8 | 3,2 | 1,4 |
| 1,3-Propandiol | 0,7 | | |
| 2-Methyl-2-propanol | 1,5 | | 1,8 |
| 2-Propanol | 3,8 | | |

a) derived from data in Tables I to IV or Tables X to XII

b) average from both sets of results c) large

In summary the present results are consistent with expectations based on literature reports and hypotheses but because of a variety of possible contributing effects, it would be unwise to regard the present results as providing unambiguous support for literature hypotheses.

(c) Photoreduction

As shown in Table XXI below the amount of photoreduction of 2-pentanone was slightly greater in alcohol than in hydrocarbon solvents on average, although there are exceptions.

Table XXI Proportion of photoreduction of 2-pentanone in different solvents [a]

| Solvent | 2-Pentanol as % total products |
|---|---|
| Hexane | .2 |
| Dodecane | 16 |
| Hexadecane | 17 |
| "Nujol" | 26 |
| Methanol | 4 |
| Ethanol | 35 |
| 2-Methyl-2-propanol | 1 |
| 1-Heptanol | 33 |
| 2-Heptanol | 38 |
| 1-Octanol | 25 |
| 2-Octanol | 28 |
| 2,6-Dimethyl-4-heptanol | 9 |
| 1-Decanol | 24 |
| 1-Dodecanol | 24 |
| 1,2-Ethandiol | 31 |
| 1,2-Propandiol | 25 |
| Cyclohexanol | 59 |
| Benzyl alcohol | 50 [b] |

a) derived from data in Tables I and II

b) approximate

This would be expected as alcohols are known to be better hydrogen atom donors to radicals, due to the greater stability of α-hydroxyalkyl radicals as compared to simple alkyl radicals.

The importance of the stability of the solvent radical in regard to the extent of ketone photoreduction is particularly well illustrated by the following observations from Table XXI.

(i) Benzyl alcohol did not produce enough reaction for accurate measurements, but the 2-pentanol peak was the predominant one - in accordance with the particularly stable character of the benzylic radical formed.

(ii) There is a greater proportion of 2-pentanol formed in irradiations of 2-pentanone in secondary alcohol solvents as compared to primary alcohol solvents.

(iii) There is little hydrogen abstraction (i.e. 2-pentanol formation) from 2-methyl-2-propanol which has no α-hydrogen atoms [149].

The yield of 2-pentanol appears to increase with increasing hydrocarbon chain length. The 2-pentanol yield in "Nujol" is comparable to that in the long chain alcohols - as would be expected. A possible explanation is suggested in the next section (Discussion, section D2).

The oxidation (hydrogen abstracted) products of the solvent formed with the ketone photoreduction product were not generally sought for. Two observations were made, however. Firstly, in the case of 2-propanol as solvent, the abnormally high acetone/cyclobutanol ratio (Table XX) or acetone yield (Taule II) is presumably due to the formation of additional acetone by oxidation of the 2-propanol (e.g. Pitts [150]). Secondly, ethanal was identified in the photolysates of all three ketones in ethanol and 1,2-ethandiol.

Ethanal is of course a possible Type I photolysis product from all three ketones, but it is only in these two solvents that a significant amount is obtained. This suggests that it is largely formed by another route in these solvents, e.g. by oxidation of the solvent. In the case of ethanol this is readily visualised as in Scheme XX, where $X^{\bullet}$ is any radical in the reaction mixture. In the case of 1,2-ethandiol an analogous sequence of reactions could lead to glycolaldehyde. No attempt to establish the presence or absence of this product was made so it could have been formed. However, ethanal, if it was correctly identified, must be formed by a different route. The following scheme (Scheme XX1) is a possibility. The compound HX is any hydrogen atom donor in the reaction mixture.

Scheme XX

$$RCOR_1 + C_2H_5OH \xrightarrow{h\nu} R\overset{\bullet}{C}(OH)R_1 + CH_3\dot{C}HOH$$

$$CH_3\dot{C}HOH + X^{\bullet} \longrightarrow CH_3CHO + HX$$

Scheme XX1

$$RCOR_1 + HOCH_2CH_2OH \xrightarrow{h\nu} R\overset{\bullet}{C}(OH)R_1 + HOCH_2\dot{C}HOH$$

$$HO\dot{C}H_2CHOH \longrightarrow {}^{\bullet}CH_2CH{=}O + H_2O$$

$${}^{\bullet}CH_2CHO + HX \longrightarrow CH_3CHO + X^{\bullet}$$

The formation of a $\dot{C}H_2CHO$ radical is not unknown. In one article Livingston and Zeldes studied the u.v. photolysis of a solution of 1% hydrogen peroxide in 1,2-ethandiol with varying amounts of water and in the presence or absence of acid catalyst [149]. The solution was purged of oxygen so $^{\cdot}OH$ radicals were produced only from the hydrogen peroxide. These then abstracted a hydrogen atom from the solvent. The solvent radicals thus formed were observed by e.s.r. spectroscopy and in the acid catalysed spectra, the major radical was $\dot{C}H_2CHO$. With no acid catalyst present the major radical produced was $HO\dot{C}HCH_2OH$ but some $\dot{C}H_2CHO$ was still formed. Other authors have also reported the formation of the $\dot{C}H_2CHO$ radical from 1,2-ethandiol, but using strong acid or base catalysed oxidation [151].

2. Viscosity of the Solvent

The results obtained for irradiations performed in hydrocarbons are the only ones likely to be of value in discussing viscosity effects, since there are too many other factors influencing the results obtained for irradiations in the alcohol solvents. It was initially considered that as the hydrocarbon chain length or the viscosity increased, the increased "internal pressure" of the system might favour the cyclization over the elimination reaction. This would be reflected in a decreasing acetone/cyclobutanol ratio with increasing solvent viscosity. As can be seen from Table XXII (page 110) this explanation is clearly not confirmed.

From Table XXII it can be seen that the percentages of acetone and cyclobutanol show a small, general decrease as the hydrocarbon chain length increases although there is considerable scatter in the data. The decrease in the acetone (elimination) yield is on the whole more marked than that of the cyclobutanol (cyclization) yield

Table XXII Percentages of the main components in the photoreaction mixtures from irradiation of the three ketones [a] in hydrocarbon solvents

| Solvent | Acetone [b] (Ac) | | | Cyclobutanol [b] (cb) | | | Ketone [b] | | | Reduced ketone | | Ac/cb | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2P | 4M2P | 2H | 2P | 4M2P | 2H | 2P | 4M2P | 2H | 2P [c] | 2H [d] | 2P | 4M2P | 2H |
| Hexane | 18 | 38 | 17 | 17 | 12 | 15 | 44 | 50 | 68 | 12 | 4 | 1,1 | 3,0 | 1,1 |
| | 21 | 30 | | 22 | 9 | | 45 | 61 | | - | | 0,93 | 3,5 | |
| Dodecane | 19 | 27 | 16 | 15 | 7 | - | 56 | 62 | 75 | 16 | 4 | 1,2 | 3,7 | - |
| Hexadecane | 15 | 25 | 17 | 14 | 6 | 13 | 46 | 66 | 69 | 17 | 4 | 1,0 | 4,1 | 1,3 |
| "Nujol" | 12 | 20 | 13 | 11 | 10 | 14 | 53 | 65 | 71 | 26 | 6 | 1,0 | 1,9 | 0,96 |

a) 2P = 2-pentanone, 4M2P = 4-methyl-2-pentanone, 2H = 2-hexanone

b) percent of total components from Tables X to XII

c) percent total products from Tables I and XX

d) percent total products from Table IV

though. It can also be seen that both the amount of remaining ketone and the yield of reduced ketone show an increase with increasing hydrocarbon chain length.

A tentative explanation for these observations may be based on consideration of the effect of the medium on the rate of rotation in the 1,4-biradical. Brown has suggested that rotation in the 1,4-biradical may be retarded in viscous media [126] and therefore this may lead to increased efficiency of back donation of the γ-hydrogen atom in such media (see introduction, sections D2(e) and E3(b)). There seems no reason to expect any direct effect of solvent viscosity in the photoreduction and the small increase in the proportion of this product may simply indicate its greater probability of occurrence when the alternative reactions (which require internal rotation) are retarded.

It could also be argued that the increased proportion of unchanged ketone might be due to a decrease in the quantum yield of the Type I reaction by increased cage recombination, with increasing solvent viscosity. There is no qualitative evidence for this in the results although it cannot be ruled out as a contributory factor. With the limited experimental evidence at hand, it seems most economical to tentatively adopt the explanation advanced in the previous paragraph.

In conclusion it must be noted that the solvent viscosity effects observed in the present work are small and that more accurate experiments on a wider range of ketones are needed to establish their validity unambiguously.

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time, an increase in triplet energy or an increase in the $\pi\pi^*$ character of the excited state. The simplest and most attractive explanation is that hydrogen abstraction from the solvent is hindered by α-substituents *.

Tributylstannane has also been used in an attempt to trap long-lived biradicals formed by intramolecular γ-hydrogen abstraction in triplet aryl alkyl ketones [60]. All attempts at trapping these biradicals with tributylstannane failed, however, [41] and from subsequent work by Wagner and coworkers [60], it appears that this is because the very rapid reduction of the triplet ketone obscures the effect. In this later work, Wagner and coworkers using alkylthiols were able to demonstrate trapping of biradicals and placed an upper limit of $2 \times 10^{-7}$ sec on the lifetime of the unsolvated biradical derived from triplet valerophenone in heptane solution. In benzene containing pyridine this lifetime was increased to $\geq 10^{-6}$ sec by solvation [60] (see below).

2. Solvent Polarity Effects

Wagner has investigated the effect of solvent polarity on the quantum yields of Type II reaction and cyclobutanol formation [35]. Aryl alkyl ketones were used since they react largely from the triplet-derived biradical [40,41,50]. Wagner found that the quantum yields of the elimination and cyclization products increased in polar solvents. He advanced the theory that hydrogen bonding

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* It is interesting to note that Lewis also suggests the hydrol (a) is formed by disproportionation of two ketyl radicals and not by disproportion of the original ketyl-solvent radical pair (from point (V)).