sium ferrioxalate[41] or benzophenone-benzhydrol[42] actinometers were employed as indicated in Table II. For ketones **1**, **5**, and **7**, the quantum yields for cyclic acetal formation were determined directly by vpc. For ketone **10**, the quantum yield for formation of **11** was equated to the quantum yield for disappearance of **10** since the reaction appears to be quantitative. The latter quantum yield was determined by the decrease in absorption of **10** at 3230 Å following irradiation.

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(41) See Table II, footnote *a*.

(42) See Table II, footnote *b*.

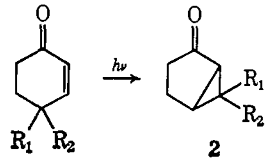
The Mechanism of Photoisomerization of Cyclohexenones. 10-Hydroxymethyl-$\Delta^{1,9}$-2-octalone. The Question of Hydrogen Abstraction from Benzene by Ketone Triplets[1-3]

David I. Schuster[4] and Donald F. Brizzolara[5]

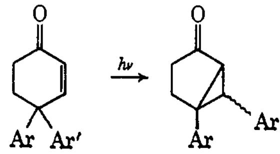
Contribution from the Department of Chemistry, New York University, University Heights, New York, New York 10453. *Received October 14, 1969*

Abstract: The photochemistry of 10-hydroxymethyl-$\Delta^{1,9}$-2-octalone (**10**) has been studied in detail. Irradiation through Pyrex in *t*-butyl alcohol gives solely and inefficiently lumiketone **11**. In chloroform, toluene, cumene, and benzene, a novel fragmentation reaction occurs in addition to give $\Delta^{9,10}$-2-octalone (**12**) and $\Delta^{1,9}$-2-octalone (**13**) and other products derived from them, as well as products derived from solvent radicals. Quenching and sensitization results indicate that all products are derived from the same radical-like triplet excited state, which is concluded to be the n,π^* triplet. It is concluded that zwitterion intermediates are not involved in any of the photochemical reactions of **10**. Solvent effects on quantum yields are attributed to stabilization of a higher π,π^* triplet and/or to complexing with the hydroxyl group of **10**. A comparison with results obtained by others with other model cyclohexenones is made, and differences in mechanistic conclusions are indicated. The inefficiency of these photochemical reactions is emphasized, and an explanation is proposed involving formation of a biradical intermediate which can regenerate the starting ketone in its ground electronic state. The results in benzene would seem to indicate that hydrogen abstraction is occurring with the same rate constant as in toluene. However, the results are shown to be consistent with an alternative mechanism involving initial addition of the triplet to benzene to form a diradical, followed by fragmentation and coupling reactions. Such a scheme is considered to be energetically more reasonable than the abstraction reaction, and consistent with results of pulse radiolysis studies in benzene and studies of hydrogen donor reactivities.

The light-induced photoisomerization (type A rearrangement) of cyclohexenones **1** to bicyclo[3.1.0]hexanones **2** is well documented.[6-11] There are also numerous examples of a second type of structural rearrangement which occurs with 4,4-diaryl- and 4,5-diarylcyclohexenones, where reaction is accompanied by migration of an aryl group (**3** → **4**).[12] Detailed mechanistic studies of the type A rearrangement have been very limited, while the aryl migration route has been elucidated in minute detail.[12] The rearrangements in *t*-butyl alcohol of phenanthrone **5** and octalone **7** to lumiketones **6** and **8**, respectively, have low quantum efficiencies; these reactions could be effected by triplet sensitization without appreciable increase in quantum efficiency, and could be quenched by piperylene, naphthalene, and di-*t*-butyl nitroxide in low concentrations.[9,10] In isopropyl alcohol, **5** gave pinacol **9** in



1 **2**



3 **4**

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[1] Part XXII of a series on the photochemistry of unsaturated ketones in solution. Part XXI: D. I. Schuster and N. K. Lau, *Mol. Photochem.*, 1, 415(1969).

[2] Supported by the U. S. Army Research Office (Durham) and in initial stages by an Institutional Grant from the National Science Foundation.

[3] Portions of this work were communicated earlier: D. I. Schuster and D. F. Brizzolara, *Chem. Commun.*, 1158 (1967).

[4] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[5] National Science Foundation Summer Fellow, 1966, and Graduate Trainee, 1967–1968.

[6] W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *J. Amer. Chem. Soc.*, 84, 2268 (1962).

[7] O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963).

[8] B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 46, 2473 (1963).

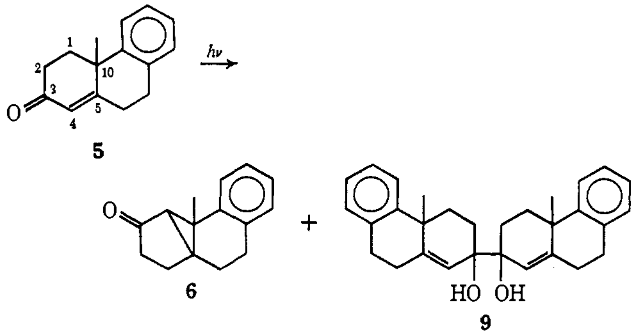
[9] H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, **88**, 1965 (1966).

[10] O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *ibid.*, **88**, 161 (1966).

[11] W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, 33, 4060 (1968).

[12] H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964); H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *ibid.*, **87**, 1138 (1965); H. E. Zimmerman and D. J. Sam, *ibid.*, **88**, 4905 (1966); H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967); H. E. Zimmerman and J. O. Grunewald, *ibid.*, **89**, 5163 (1967); H. E. Zimmerman and R. L. Morse, *ibid.*, **90**, 954 (1968); H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3749 (1968); H. E. Zimmerman and N. Lewin, *ibid.*, **91**, 879 (1969); H. E. Zimmerman and W. R. Elser, *ibid.*, **91**, 887 (1969).

addition to lumiketone **6**, and formation of both products was quenched by naphthalene.[9] The reaction of chiral **5** proceeded with a minimum of 95% retention of optical activity.[10]



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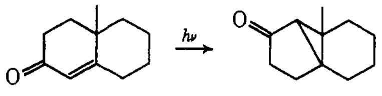
9



7

8

The proposed mechanism[9] for isomerization of **5** and **7** involves 1,10 σ-bond cleavage of the n,π^* triplet state with formation of a diradical species, followed by geometrical reorganization and rebonding to give the product.

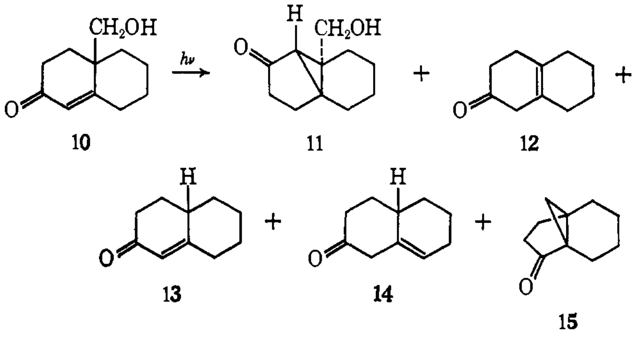
The success of the radical fragmentation reaction as a probe into the nature of the reactive intermediates involved in cyclohexadienone rearrangements[13] prompted study of a cyclohexenone derivative which could undergo a radical fragmentation reaction in competition with the usual type A lumiketone rearrangement. The expectation that 10-hydroxymethyl-$\Delta^{1,9}$-2-octalone (**10**) would fulfill these conditions was completely realized.

Results

Synthesis of 10. The original procedure for synthesis of **10**[14] was modified and an alternative route based on work of Stork, *et al.*,[15] was developed. See the Experimental Section for details.

Photolysis Products. Irradiation of **10** in *t*-butyl alcohol through Pyrex proceeded very slowly to give only one isolable product. After 300 hr, 50% unreacted starting material remained. The product, isolated by preparative gas–liquid chromatography (glpc), had infrared bands at 3550, 3400 (hydroxyl), and 1710 cm^{-1}, the latter characteristic of the carbonyl group of a bicyclo[3.1.0]hexan-2-one.[16] The uv spectrum showed only end absorption. In the nmr spectrum, there were no vinyl proton resonances, and the resonance at δ 3.67 (same as in **10**) was characteristic of the methylene protons of the hydroxymethyl group. The mass spectrum had a molecular ion at *m/e* 180 and major fragments at 150 and 149 from loss of CH_2O and CH_2OH, respectively. The data (see Experimental Section for details) indicate that the photolysis product is the lumiketone **11**.

Photolysis in chloroform gave several products in addition to **11**, which were identified as compounds **12**, **13**, **14**, and **15**. These compounds, the anticipated products of the fragmentation reaction, were independently synthesized (see Experimental Section) and compared directly with the photolysis products by glpc coinjection techniques, as well as spectrally. Compound **15** is a known product of photolysis of **12** and was synthesized for comparison from **12**.[17] Hexachloroethane was also isolated and identified as above by comparison with authentic material.



10 **11** **12** **13** **14** **15**

In toluene, cumene, and benzene, photolysis of **10** gave the same products: lumiketone **11**, the β,γ-unsaturated ketone **12** and its photolysis product **15**. In the toluene reactions, bibenzyl was also formed, while biphenyl was identified as a product from the benzene reactions.

Table I summarizes representative yields of products in each of the solvents studied, as determined by glpc using benzil and acenaphthene as internal standards.

Table I. Products from Photolysis of Octalone **10**

Solvent	Irradiation time, hr	Yield, %[a]					
		10	11	12	13	14	15
Chloroform	4	26	4	2	20	6	5
Toluene	10	17	15	8	0	0	3
Cumene	10	25	9	6	0	0	4
Benzene	10	23	19	11	0	0	3
t-Butyl alcohol	600	25	45	0	0	0	0

[a] Percentage of initial amount of **10**, determined by glpc using benzil and acenaphthene as internal standards. The balance of the starting material probably results in higher molecular weight compounds which do not appear in the vapor chromatogram and which could not be isolated by column chromatography.

Quantum Yields. The quantum yields for disappearance of octalone **10** as well as formation of products **11** and **12** in benzene were directly measured at 313 nm using ferrioxalate actinometry.[18] The data in the other solvents were obtained by competitive irradiation of **10** in several solvents, including benzene, in a merry-go-round apparatus in which all tubes received the same amount of light. The data were corrected for the differences in light absorption in each solvent tube on the basis of the integrated absorption spectra

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(13) D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **90**, 5145 (1968); D. J. Patel, and D. I. Schuster, *ibid.*, **90**, 5137 (1968).

(14) L. S. Minckler, A. S. Hussey, and R. H. Baker, *ibid.*, **78**, 1009 (1956).

(15) G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *ibid.*, **87**, 275 (1965).

(16) J. Frei, C. Ganter, D. Kägi, K. Kocsis, M. Miljković, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1049 (1966).

(17) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194 (1967); J. R. Williams and H. Ziffer, *Tetrahedron*, **24**, 6725 (1968).

(18) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

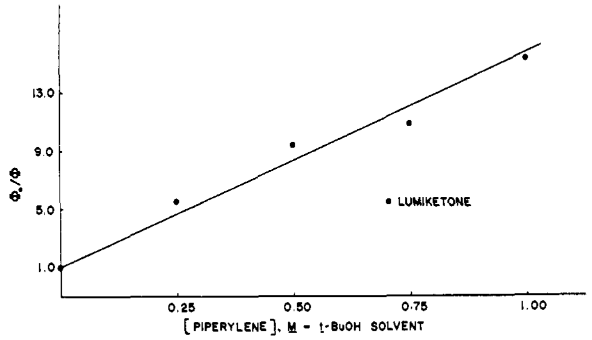

Figure 1. Stern–Volmer quenching plot for formation of lumiketone **11** in *t*-butyl alcohol as a function of piperylene concentration.

and the spectral distribution of the lamp.[19] The corrected data are given in Table II.

Table II. Quantum Yields at 313 nm

Solvent	$\phi_K \times 10^3$ [a]	$\phi_{lumi} \times 10^3$ [b]	$\phi_{octalone} \times 10^3$ [c]
Benzene	8.0	2.9	1.1
Benzene-d_6	8.3	2.6	*d*
Toluene	8.1	2.8	1.1
t-Butyl alcohol	1.1	0.2	0.0

[a] ϕ for disappearance of ketone **10**. [b] ϕ for appearance of ketone **11**. [c] ϕ for appearance of octalone **12**. [d] See Discussion in text.

Sensitization and Quenching Experiments. Qualitative triplet sensitization of the photoreaction of **10** in toluene was observed using benzophenone and acetophenone, which absorbed, respectively, 91 and 96% of the incident light. The glpc tracings could not be quantitatively analyzed because of peaks due to sensitizer and sensitizer products.

Quenching of the reactions of **10** in benzene, toluene, and *t*-butyl alcohol with piperylene was observed, and the corresponding Stern–Volmer plots are given in Figures 1, 2, and 3. Analysis by glpc indicated extraneous peaks, which were shown to be derived from reaction of piperylene with **10** but not with the reaction products. As quenching experiments were run to low conversions, errors due to formation of these products (probably adducts) were very small.

The Stern–Volmer relationship for formation of products **11** and **12** is given by eq 1, where k_r is the rate constant for unimolecular rearrangement of the triplet, k_a the rate constant for hydrogen abstraction which leads ultimately to **12** (see below), and k_d the sum of the rate constants for all deactivation pathways for the triplet

$$\phi_0/\phi = 1 + k_q\tau_0[Q] = 1 + \frac{k_q[Q]}{k_r + k_d + k_a[RH]} \quad (1)$$

The quantum yields for formation of **11** and **12** are given by eq 2 and 3, respectively, where A is the efficiency of triplet formation by intersystem crossing from the singlet

$$\phi_{lumi} = \frac{Ak_r}{k_r + k_d + k_a[RH]} = Ak_r\tau_0 \quad (2)$$

$$\phi_{octalone} = \frac{Ak_a[RH]}{k_r + k_d + k_a[RH]} = Ak_a[RH]\tau_0 \quad (3)$$

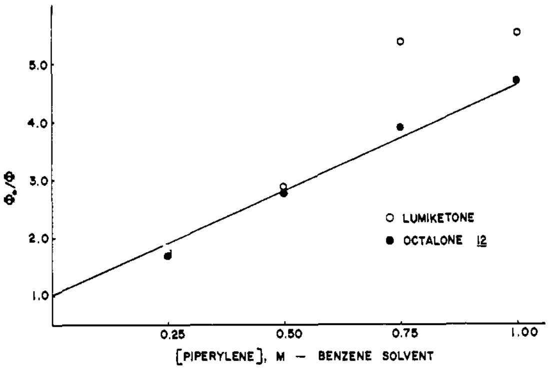

Figure 2. Stern–Volmer quenching plot for formation of lumiketone **11**, ○, and octalone **12**, ●, in benzene solution as a function of piperylene concentration.

It is assumed that A is unity, on the basis of the linearity of the Stern–Volmer plots, and the observation that quantum yields for disappearance of cyclohexenones are not substantially increased in sensitized *vs.* unsensitized photolyses.[9,10] The Stern–Volmer slopes and standard deviations given in Table III were calculated by a least-squares computer program. The rate constants in Table III and the triplet lifetimes were calculated taking k_q in benzene as $5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ and assuming all inefficiency comes from triplet deactivation. An alternative to this usual assumption is discussed later. Parameters in solvents other than benzene were calculated assuming an inverse dependence of k_q on solvent viscosity, using the benzene value as the standard. The reproducibility of the Stern–Volmer data was slightly outside the deviations indicated in Table III, so that the slopes and rate constants are considered to be reproducible within 10%.

Kinetic Studies. In order to determine the role of benzene and toluene in the photoreactions of octalone **10**, photolyses were performed in benzene–*t*-BuOH and toluene–*t*-BuOH mixtures on the merry-go-round apparatus. Quantum yields for disappearance of **10** and formation of **11** and **12** were independently determined, relative to the data for the pure solvents.[19] The data demonstrate a linear dependence of $1/\phi$ for each process *vs.* the inverse concentration of the aromatic solvent. The data for formation of octalone **12** are presented graphically in Figure 4. Using benzene-d_6 in place of benzene, it was seen that the overall isotope effect on the disappearance of starting material appears almost entirely in the reaction leading to **12**. From the slopes of the lines in Figure 4, using eq 4 and assuming k_r and k_d are the same in benzene and benzene-d_6 (see Table I), one finds that $k_{a_{benzene}}/k_{a_{benzene\text{-}d_6}} = 1.95$.

$$\frac{1}{\phi_{oct}} = \frac{1}{A}\left(1 + \frac{k_d + k_r}{k_a[RH]}\right) \quad (4)$$

To determine if the starting material **10** were acting as a hydrogen donor to the excited triplet, the ratio of **11**/**12** was determined at different concentrations of **10**. The product ratio should increase markedly with decreasing concentration of **10** if **10** were acting in this capacity. The ratio **11**/**12** was 3.5 at $3.66 \times 10^{-2}\ M$ **10** in benzene, and 3.85 at $2.8 \times 10^{-3}\ M$ **10** in benzene. Within an estimated accuracy for this determination of

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(19) For details, see D. F. Brizzolara, Ph.D. Dissertation, New York University, 1968.

Table III. Stern–Volmer Slopes, Triplet Lifetimes, and Rate Constants

Solvent	Product	$k_q\tau_0$	$\tau_0 \times 10^9$, sec	k_r, sec^{-1}	k_d, sec^{-1}	k_a, M^{-1} sec^{-1}
Benzene	**11**	5.1 ± 0.8	1.0	2.9×10^6	9.8×10^8	
Benzene	**12**	3.8 ± 0.2	0.8		1.3×10^9	1.3×10^5
Toluene	**11**	7.3 ± 0.5	1.2	2.3×10^6	8.6×10^8	
Toluene	**12**	5.9 ± 0.4	0.9		1.1×10^9	1.2×10^5
t-BuOH	**11**	13.5 ± 1.2	5.9	3.4×10^4	1.7×10^8	

about 10%, the product ratio is concluded to be invariant with the concentration of ketone **10**.

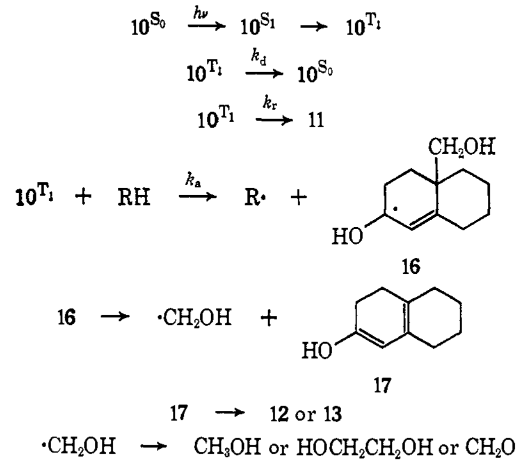
Miscellaneous Experiments. Lumiketone **11** was irradiated as per the conditions used for study of **10** in chloroform, benzene, and toluene. Octalones **12**, **13**, and **14** were not formed in any of these reactions. Bibenzyl and hexachloroethane were produced in toluene and chloroform, respectively. An unidentified product in toluene corresponded to a product formed on prolonged irradiation of **10** in toluene.

The expected products derived from the hydroxymethyl group lost on formation of ketones **12–15** are methanol, ethylene glycol, and formaldehyde. Direct determination of these products provided formidable analytical problems, and it was more convenient to analyze for these compounds as the dimedone derivative (formaldehyde) and the trimethylsilyl derivatives (methanol and ethylene glycol). In toluene, approximately 10–20% of the theoretical amount of the formaldehyde derivative was formed, and a small amount (<5%) of the ethylene glycol derivative.[19] While a measurable amount of the methanol derivative was formed, an accurate quantitative estimate was impossible because of analytical difficulties (see ref 19).

Discussion

Proposed Mechanism for Photolysis of Octalone 10. The results will first be discussed within the framework of a proposed mechanism for photolysis of **10**, shown in Chart I. After excitation and intersystem crossing to the triplet state of **10**, there is a competition between rearrangement of the triplet to give **11**, deactivation of the triplet, and hydrogen abstraction to give the ketyl radical **16**. The radical **16** can lose a hydroxymethyl radical to generate enol **17**, which can give **12** or **13** directly on ketonization. The fact that no fragmentation is observed in *t*-butyl alcohol, a poor hydrogen donor toward radicals, suggests that hydrogen abstraction precedes fragmentation,[13] although the reverse was an *a priori* possibility. The surprising reactivity of benzene as an apparent hydrogen donor will be discussed in detail below.

Chart I



In toluene and cumene photolyses, only the β,γ-octalone **12** and its photoproduct **15** are formed, while in chloroform two other octalones **13** and **14** are formed. It was observed that the amount of the conjugated octalone **13** formed increases with time of photolysis at the expense of **12** and **14**. This gradual increase in the percentage of the thermodynamically more stable isomer suggests that conditions of thermodynamic control of product distribution are prevailing. One possibility is that a radical species generated in chloroform can cause isomerization of the products. Perhaps the trichloromethyl radical because of its longer lifetime is able to catalyze the isomerization by addition and abstraction reactions better than the more reactive shorter lived benzylic radicals.

The formation of hexachloroethane and bibenzyl in chloroform and toluene photolyses occur from dimerization, respectively, of the trichloromethyl and benzyl radicals, which must have arisen from hydrogen abstraction from solvent by a triplet. This definitely indicates radical character in the reactive triplet state. The formation of methanol and ethylene glycol can be reasonably explained only from the hydroxymethyl radical, formed from fragmentation of the radical **16**. These reactions are analogous to the observation of pinacol (**9**) formation from photolysis of phenanthrone **5**.[9] None of these reactions can be satisfactorily rationalized on the assumption that the triplet state is zwitterionic in character, or that zwitterions are involved at any stage of the reaction.[20]

In order for these conclusions to be valid for the rearrangement reaction as well, it is necessary that the triplet leading to fragmentation is the same one that rearranges. Although Figure 3 indicates a slightly larger Stern–Volmer slope for quenching of lumiketone as compared with octalone formation, the data as summarized in Table III clearly indicate that the lifetimes of the triplet state leading to each product are in fact the same, within an experimental error of about 10%. It is therefore concluded that, on the basis of present evidence, all of the reactions in this system proceed from one and the same excited triplet state, or from two nearly isoenergetic states which are in thermal equilibrium at room temperature.[21,22] Thus, the

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[20] For review of the literature and discussion of this point, see P. J. Kropp, *Org. Photochem.*, 1, 1 (1967).

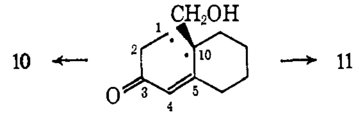
[21] It should be noted that the glpc analyses for quenching of formation of octalone 12 are probably subject to a larger error than those for lumiketone 11 formation, because of partial overlap with the other peaks in the chromatogram, especially at high quencher concentrations.

[22] Although Stern–Volmer plots were not presented, it is claimed in ref 9 that formation of pinacol and lumiketone on photolysis of 5 in isopropyl alcohol proceed from the same excited triplet, or two rapidly equilibrating triplets.

conclusion above with respect to the absence of zwitterionic character in the precursor of the fragmentation reaction holds for the lumirearrangement as well.

The low efficiency of the photoconversions of **10** is analogous to that observed in previous studies of cyclohexenones, where ϕ is always on the order of 0.001–0.01. The inefficiency of reaction has been attributed to rapid deactivation of cyclohexenone triplets to the ground state radiationlessly.[9] The consequence of this assumption is that the calculated rate constants for unimolecular isomerization of the triplet come out to be on the order of 10^5–10^6 sec^{-1}, three to four orders of magnitude less than that for analogous cyclohexadienones.[9] However, it is difficult to understand why radiationless decay rates for cyclohexenone triplets should be as great as 10^9 sec^{-1}, while values for almost all other excited triplets, ketone as well as hydrocarbon, are usually not greater than 2–3 × 10^5 sec^{-1} in solution.[23] A decay rate in excess of 10^6 sec^{-1} is indicative of rapid and efficient reaction of the excited state to give an intermediate which can regenerate starting material in its ground state in competition with other modes of reaction.[23] The formation of intermediate biradicals has recently been proposed to explain the inefficiency of photoreactions of cyclohexanones and cyclopentanones in solution.[24a] It has also been suggested that inefficiency in reactions of cyclohexenones is due to rapid irreversible decay of the triplet to a twisted ground state.[24b] Rate constants for deactivation of cyclohexenone itself[24b] and simple substituted cyclohexenones[12] are greater than for some fused ring cyclohexenones,[9] *e.g.*, **5** and **7**, consistent with this explanation. However, the rate constants for deactivation of triplet **10** (k_d in Table III) are even larger than for simple cyclohexenones, suggesting that decay of the triplet to a twisted species may not be the correct or the entire explanation, at least in this case.

One possibility is that the triplet excited state of **10** opens to give a diradical **18**, which preferentially recyclyzes to give **10** in its ground state, in competition with the alternative mode of cyclization to **11**. Arguing against this postulate is the observation of retention of optical activity in the conversion of chiral **5** to **6**,[10] and also the stereospecificity of rearrangement of the 1α-deuterated ketone **19b** to the corresponding lumiketone.[25] Examination of molecular models clearly indicates, however, that the angular methyl or hydroxymethyl group in **5**, **10**, **19** and related compounds would strongly inhibit the rotation that is necessary for formation of the new 1,5-bond in the lumiketone from other than the bottom side of the molecule. Thus, stereospecificity of the rearrangement is to be expected in these molecules purely on steric grounds, and does not eliminate the possibility of rearrangement in two steps. Formation of a diradical in which carbons 1, 2, 3, 4, 5, and 10 lie in a plane is unlikely according to the models. Further experiments are necessary, however, to determine whether any reversible ring cleavage is operative in cyclohexenone photolyses in this and related systems.[25a,26]



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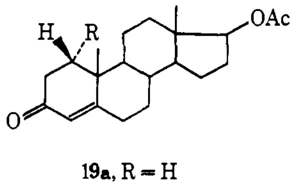


19a, R = H
b, R = D

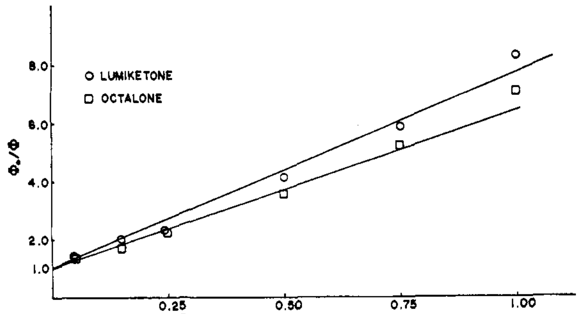
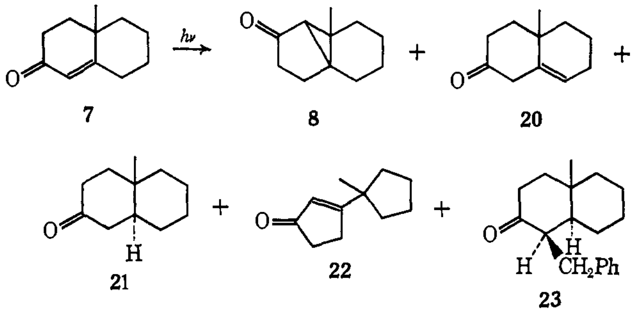


Figure 3. Stern–Volmer quenching plot for formation of lumiketone **11**, ○, and octalone **12**, □, in toluene solution as a function of piperylene concentration.

A detailed investigation of the photochemistry of the parent octalone **7** and the steroid enone **19** has recently been reported by Bellus, Kearns, and Schaffner (BKS),[25] and some of their conclusions are at variance with those given above. Since **7** and **19** behave similarly, the discussion will be confined to **7**, which on photolysis gives **8**, **20**, **21**, **22**, and **23** (in toluene).[25] Isomerization to **8** and **20** and reduction to **21** were observed in seven



7 **8** **20**

21 **22** **23**

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(23) P. J. Wagner, *J. Amer. Chem. Soc.*, **88**, 5672 (1966); P. J. Wagner, *Mol. Photochem.*, **1**, 71 (1969). These papers present a discussion of this point with other pertinent references.

(24) (a) P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969); (b) P. J. Wagner and D. J. Bucheck, *ibid.*, **91**, 5090 (1969).

(25) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).

(25a) NOTE ADDED IN PROOF. It is possible that in diradical **18**, overlap of orbitals on C_1, C_4, C_5, and C_{10} prevents rotation around C_1–C_2 and allows retention of stereochemistry. Also, stretching of the C_1–C_{10} bond without formation of a discrete diradical such as **18**, perhaps accompanied by twisting around the double bond,[24b] may be a route for energy loss competitive with product formation. That is, deactivation and rearrangement may be structurally related, as postulated for some cyclohexadienones [H. E. Zimmerman and G. Jones II, *J. Amer. Chem. Soc.*, **92**, 2753 (1970)]. In any event, decay to the ground state in these systems probably occurs from a relaxed triplet of different geometry than the ground state, a triplet which *may* be quite different in structure and energy from that responsible for phosphorescence at low temperature.[27]

(26) (a) If the predominant triplet process is cleavage of the 1,10-bond, then the triplet lifetime would be determined almost entirely by the rate of this reaction, *i.e.*, $1/\tau = k_r + k_a[\mathrm{RH}]$. The quenching data on this basis would yield values of k_r on the order of 10^9 sec^{-1}, comparable with those for cyclohexadienones,[9,13,26b] in contrast with some earlier conclusions regarding differences in reactivity in these two types of systems.[9,10] (b) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967).

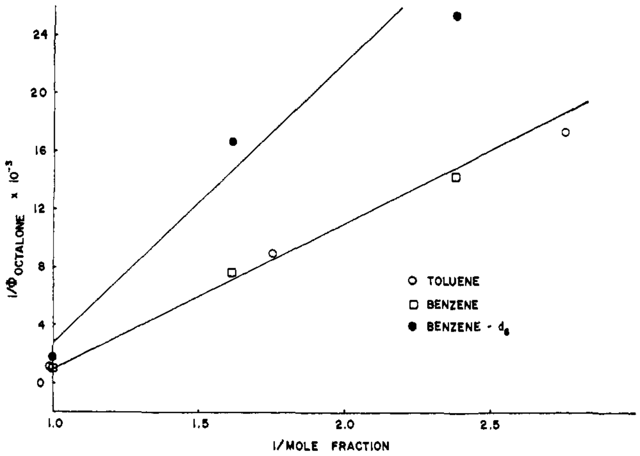
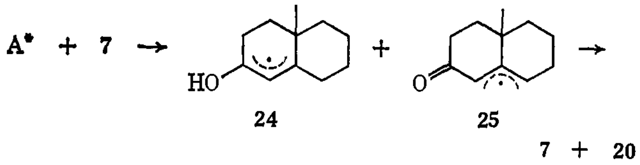


Figure 4. Variation in quantum yield for formation of octalone **12** in *t*-butyl alcohol as a function of the mole fraction of added toluene, ○, benzene, □, and benzene-d_6, ●.

solvents. The conversion of **7** to all products could be effected by triplet sensitization. Quenching experiments indicated that all products other than **20** arose from the same triplet state. Kinetic studies indicated a bimolecular reaction for isomerization to **20**, the rate dependent on the concentration of **7**. The reverse photochemical reaction, **8** → **7**, was also observed. The results were interpreted by BKS[25] in terms of two reactive triplets, one (A) responsible for isomerization to **20**, and the other (B) responsible for the remaining reactions. It was concluded that B is the lower energy triplet in alcohol solution, and has a π,π^* configuration. The formation of **20** in alcohol was envisaged from an upper n,π^* triplet (A) *via* H abstraction on oxygen from **7** (ground state) to give a radical pair **24** and **25**, which disproportionate to **7** and **20** in their ground states (see below). From singlet → triplet absorption and phosphorescence excitation measurements on a series of α,β-unsaturated ketones, including **19**, in 2-methyltetrahydrofuran, such an ordering of triplet states was also indicated, with $E_T(n,\pi^*) > E_T(\pi,\pi^*)$.[27]



24 **25**

7 + **20**

On the assumption that hydrogen abstraction on oxygen is a characteristic reaction of n,π^* triplets,[25,28] the reactive triplet in the case of **10** which leads to abstraction as well as rearrangement reactions is concluded to be an n,π^* triplet. It is likely that in cyclohexenones the two lowest triplets, n,π^* and π,π^*, are close in energy,[27] and that their energy separation is solvent dependent. A reversal in the order of these triplets for the cases of **7** and **19** was postulated by BKS[25] in hydrocarbon as compared with alcohol solvents. They concluded, however, that the rearrangement to lumiketone proceeded from the π,π^* triplet even when this was not the lowest triplet. There is nothing in our data for **10** which requires or compels such a conclusion, and all the data are compatible with a simple scheme (Chart I) in which all reactions proceed *via* a single n,π^* triplet state, or two triplet states of mixed configurations which are sufficiently close in energy to be at thermal equilibrium at room temperature. The difference in interpretation in the two systems is striking, considering that the triplet lifetimes from comparable quenching data in the same solvent (benzene) are so similar: the Stern–Volmer slope ($k_q\tau$) for naphthalene quenching of **7** → **8** is 10.0, while that for piperylene quenching of **10** → **11** is 5.1. Quantum efficiencies for disappearance of **10** (0.0011), **5** (0.0084),[9] and **7** (0.0038)[9] are also comparable. The differences in proposed mechanism in these systems must at present remain unresolved, in the absence of further photochemical data and spectroscopic studies on both **7** and **10**.[29–31]

Reactions in Benzene. An Alternative to Hydrogen Abstraction. The results obtained from photolysis of **10** in benzene are most surprising. The fragmentation reaction was observed, and the quantum efficiency and rate constant k_a were not significantly different in benzene from that in toluene, a good hydrogen donor. The kinetic dependence on the benzene concentration expected if the triplet reacted with benzene was observed (Figure 4). The possibility that the triplet was reacting with a ground-state ketone molecule in benzene was eliminated. Finally, using benzene-d_6, a kinetic isotope effect k_{aH}/k_{aD} of 1.95 was observed. It was shown that the deuterium isotope effect for hydrogen abstraction from the carbinol carbon in benzhydrol and 2-propanol by benzophenone triplet was 2.7 and 2.8, respectively.[32] Thus, the results seem to indicate that hydrogen abstraction from benzene by triplet **10** is indeed occurring, and with a rate commensurate with abstraction from toluene!

While the data seem convincing, the conclusion is not satisfying. The lack of reactivity of benzene as a hydrogen donor toward free radicals is well known.[33,34]

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[27] G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **51**, 1890 (1968); D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968).

[28] The reactivity of ketone n,π^* triplets is decreased as the energy gap is decreased between it and the next higher π,π^* triplet. While π,π^* triplets may have some inherent H-abstraction reactivity, it is far less than for n,π^* triplets. For discussion and references, see N. C. Yang and R. L. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).

[29] The reactive triplet in photoisomerization of 2,5-cyclohexadienones, a reaction structurally analogous to **1** → **2**, has been shown in some cases to be the n,π^* triplet,[13,26b,30a] although such reactions *via* π,π^* triplets also seem possible.[1,30b] Spectroscopic studies of steroid dienones and related systems indicate that the lowest triplet in such systems is the π,π^* triplet (D. R. Kearns, private communication of unpublished results). See also G. Marsh, D. R. Kearns, and M. Fisch, *J. Amer. Chem. Soc.*, **92**, 2252 (1970).

[30] (a) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 6589 (1967); (b) M. H. Fisch and J. H. Richards, *ibid.*, **85**, 3029 (1963).

[31] The increase in rate as well as efficiency of isomerization of **10** on proceeding from *t*-butyl alcohol to hydrocarbon solvents (Tables II, III, and Figure 4) may be the result of several effects. Solvation of the hydroxyl group in **10** by alcohols may electronically and/or sterically retard reactions of the triplet. There may also be a reversal of the ordering of the triplets, or at least a smaller energy difference between them, in alcohol as compared with hydrocarbon solvents, as discussed above in the case of **7**.[25]

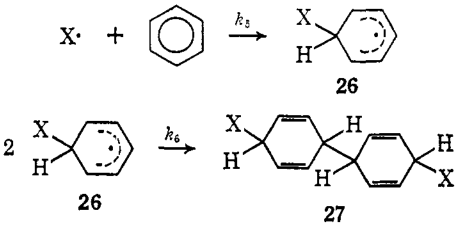
[32] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961); W. M. Moore and M. D. Ketchum, *J. Phys. Chem.*, **68**, 214 (1964).

[33] For a review of the literature see C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, especially p 491 ff. Note that the C–H bond strength in benzene is upward of 100 kcal/mol.

[34] In hydrogen abstraction by methyl radicals, benzene is 19 times less reactive than toluene and 280 times less reactive then chloroform (F. G. Edwards and F. R. Mayo, *J. Amer. Chem. Soc.*, **72**, 1265 (1950)). Moreover, since only about 25% of the methyl radicals which react with benzene end up as methane, it appears that methyl addition to the benzene ring must be the chief initial reaction, followed by dimerization and disproportionation reactions.[35]

[35] M. Levy and M. Szwarc, *ibid.*, **76**, 5981 (1954).

The lack of reactivity is supported by results from pulse radiolysis of hydrogen and water in benzene.[36,37] It was shown that the primary reaction of the very reactive hydrogen atoms and hydroxyl radicals with benzene and other aromatic molecules was not hydrogen abstraction from the ring, but addition to the ring to give substituted cyclohexadienyl radicals **26** (eq 5). In the case of hydrogen atom addition, substitution of benzene-d_6 for benzene had no effect on the rate constant k_5 within an uncertainty of 15%. The main products **27** arise from rapid combination of the cyclohexadienyl radicals, eq 6. Biphenyl and bibenzyl were produced in negligible yields in benzene and toluene runs, respectively. Even in toluene, the ratio of addition to abstraction rates was at least 6:1, and probably greater than 30:1.[36,37]



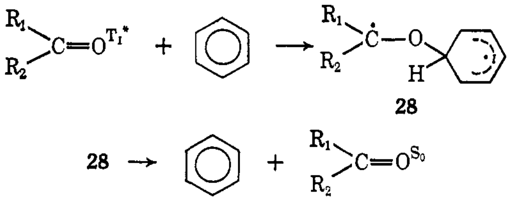
(5)

26

(6)

26 **27**

On the basis of the above, and similar results from many other studies, it is difficult to accept the conclusion that the triplet of **10** reacts with benzene by the hydrogen abstraction mechanism given in Chart I. Hydrogen abstraction from benzene by ketone triplets has been postulated a number of times in the literature.[25,38-40] In all cases, there is an alternative more plausible explanation in which the initial step, analogous to eq 5, is the addition of the triplet to benzene, as shown in eq 7, with formation of the diradical **28**.[41] Such a suggestion was made earlier by Baum and Norman,[42] on the basis of their studies of the behavior of biacetyl triplet in phenylacetic and phenoxyacetic acids. The addition (eq 7) will in most cases be reversible, in contrast with that in eq 5, with regeneration of ground-state ketone (eq 8). This would provide a mechanism for deactivation of triplets by benzene, a process known to be unusually fast and efficient[38,43,44] but for which no truly satisfactory explanation had appeared before the postulate of Baum and Norman.[42] If the adduct diradical **28** can undergo a fragmentation[41,42] or a hydrogen shift,[45] some net photoreaction can occur.[45a]



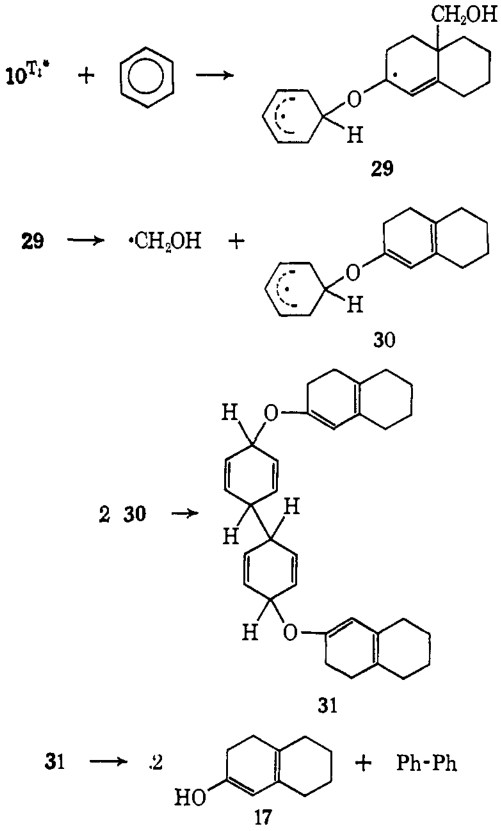
(7)

28

(8)

This postulate can be illustrated with **10** (Chart II).

Chart II



(9)

29

(10)

30

(11)

31

(12)

17

The adduct diradical **29** could fragment to give the hydroxymethyl radical and radical **30** (eq 10). Combination of two radicals **30**, analogous to the dimerization seen in pulse radiolysis (eq 6),[36,37] would give **31** (eq 11), which could thermally decompose to biphenyl and the enol **17** (eq 12), the proposed precursor of products **12** and **13**. The latter reaction has precedent in the thermal decomposition of **27** (X = OH) into water and biphenyl.[46] *Thus, the formation of biphenyl is not a priori proof of the intermediacy of phenyl radicals in such a reaction.*

The evidence is consistent with the mechanism in Chart II, which kinetically is indistinguishable from the mechanism of Chart I. The observed isotope effect,

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(36) M. C. Sauer and B. Ward, *J. Phys. Chem.*, 71, 3971 (1967), and references cited.

(37) P. Neta and L. M. Dorfman, Advances in Chemistry Series, No. 81, American Chemical Society, Washington, D. C., 1968; R. Wander, P. Neta, and L. M. Dorfman, *J. Phys. Chem.*, 72, 2946 (1968), and references cited therein.

(38) J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 528 (1963).

(39) M. B. Rubin and Z. Neuwirth-Weiss, *Chem. Commun.*, 1607 (1968).

(40) S. Kuwata and K. Schaffner, *Helv. Chim. Acta*, **52**, 173 (1969).

(41) The intramolecular attack of a ketone triplet on a benzene ring has been proposed to explain the photoisomerization of dibenzoylethylenes. The proposed intermediate is analogous to **28**. See G. W. Griffin and E. J. O'Connell, *J. Amer. Chem. Soc.*, **84**, 4148 (1962); H. E. Zimmerman, H. G. C. Durr, R. G. Lewis, and S. Bram, *ibid.*, **84**, 4149 (1962); and H. E. Zimmerman, H. G. Durr, R. S. Givens, and R. G. Lewis, *ibid.*, **89**, 1863 (1967). See also O. L. Chapman, H. G. Smith, R. W. King, D. J. Pasto, and M. R. Stoner, *ibid.*, **85**, 2031 (1963).

(42) E. J. Baum and R. O. C. Norman, *J. Chem. Soc.*, *B*, 227 (1968).

(43) C. A. Parker and T. A. Joyce, *Chem. Commun.*, 749 (1968).

(44) D. I. Schuster and M. R. Topp, unpublished results from the Royal Institution, London.

(45) Although hydrogen atom shifts in radicals are usually not observed, such shifts in diradicals are known in a number of systems. For discussion and references, see D. I. Schuster and I. S. Krull, *Mol. Photochem.*, 1, 107 (1969).

(45a) NOTE ADDED IN PROOF. We have been informed by Professor Jack Saltiel, Florida State University, of evidence accumulated in his laboratory which strongly indicates that the very inefficient reaction of benzophenone triplets with benzene to give biphenyl and benzhydrol indeed occurs *via* hydrogen abstraction from benzene. These results, however, do not bear on the main process which occurs in this system, namely deactivation of benzophenone triplets to the ground state, which may still take place according to eq 7 and eq 8, or *via* reversible charge-transfer complex formation. We are grateful for private communication of these results prior to publication.

(46) L. M. Dorfman, I. A. Taub, and R. E. Buchler, *J. Chem. Phys.*, 36, 3051 (1962).

$k_{\mathrm{H}}/k_{\mathrm{D}} = 1.95$, is at first surprising, since formation of a bond (eq 9) at an sp^2 carbon atom which changes hydrization toward sp^3 in the transition state, would be expected to give an inverse isotope effect, $k_{\mathrm{H}}/k_{\mathrm{D}} < 1$.[47,48] However, if the C–H bonds at the other carbon atoms on the benzene ring weaken in the transition state leading to diradical **29**, the isotope effects at these positions will be in the normal direction, $k_{\mathrm{H}}/k_{\mathrm{D}} > 1$.[48] The net effect is consistent with the observed value. Such a small isotope effect is unreasonable for abstraction of the very strongly bound hydrogen atom of benzene, for which an isotope effect would be expected in excess of that found for secondary alcohols ($k_{\mathrm{H}}/k_{\mathrm{D}}$ 2.7).[32]

Variants of this mechanism, starting from an adduct diradical **28**, can be written for the other reactions in which H abstraction from benzene has been postulated.[25,38–40,45a] It is possible that such a mechanism holds even for reactions with toluene, although abstraction reactions might make some contribution. Further studies are in progress[44] to distinguish between the alternatives.

Experimental Section

Spectra. Nuclear magnetic resonance spectra were taken on a Varian Associates Model A-60 spectrometer. Tetramethylsilane was used as an internal standard in most cases. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating infracord spectrophotometer. A polystyrene film was used for calibrating the spectra. Spectra of liquids were taken as thin films between salt plates or as solutions in carbon tetrachloride or chloroform. Spectra of solids were taken as solutions in carbon tetrachloride or chloroform. Ultraviolet spectra were recorded on a Cary Model 15 spectrophotometer. Mass spectra were taken at Columbia University by Miss V. Parmakovich on a Hitachi Perkin-Elmer Model RMU-6D mass spectrometer at 13 and 75 V. For spectral details, see ref 19.

Gas–Liquid Partition Chromatography (Glpc). Analytical. Glpc analyses were made using an F & M Model 810 or F & M Model 5751-A gas chromatograph. Both instruments are equipped with dual column flame ionization detection and a Disc chart integrator. Internal standards were used in quantitative experiments. The The technique involves determination of the relative detector response of the standard compound and the compound under study. Standard solutions consisted of weighed amounts of standard and compound dissolved in a suitable solvent. These solutions were then injected into the chromatograph and the peak areas were recorded, and response factors were calculated. Standard solutions were prepared for each run and were injected during each run. In this way variations in the factor were taken into account.

In a typical reaction standard was added to the reaction mixture after irradiation, some solvent was removed in a stream of dry nitrogen and the resulting solution was chromatographed. From the calculated factor, the peak areas, and the known weight of added standard, the weight of the photoproduct was determined. The column used for most of the glpc work reported was a 6 ft × $^1/_8$ in. column of 15% SE-30 on Chromosorb W, A/W DMCS. The use of other columns is indicated at the appropriate place. At a column temperature of 170°, injection port 210°, flow rate 40–60 ml/min, typical retention times were enone **10**, 12 min; lumiketone **11**, 9 min; octalone **12**, 2.8 min; octalone **13**, 3.4 min; octalone **14**, 2.3 min; ketone **15**, 2.2 min; benzil, 13.7 min; and acenaphthene, 4.7 min.

Preparative Glpc. An Aerograph Model A-700 chromatograph was used for all preparative glpc work. A 10 ft × 0.25 in. column of 15% SE-30 Chromosorb W, A/W DMCS column was used. Collections were made using an "L" tube inserted into an nmr tube appropriately cooled.

Photolysis Apparatus. Immersion Well Apparatus. This apparatus consists of a water-jacketed quartz well which houses a 450-W high-pressure mercury arc lamp (Hanovia L 679 A). The immersion well fits into a cylindrical reaction vessel which has a capacity of 325 ml. The reaction vessel is equipped with an inlet for nitrogen, an outlet fitted with a condenser, and an outlet for the removal of aliquots. The solutions were stirred with a magnetic stirring bar. The light was filtered by placing the appropriate cylindrical glass filter sleeve around the source. Alternatively, the same source was used without the reaction vessel. In this case, stoppered Pyrex tubes were placed adjacent to the immersion well.

Merry-Go-Round Apparatus. This apparatus consists of a turntable containing either six or twelve sample positions, belt driven by an electric motor. The immersion well apparatus described above fits into a cylindrical opening in the center of the turntable. In most cases the quartz well was used without a filter sleeve, the Pyrex glass of the reaction vessels serving as the filter. Use of this apparatus and uniform reaction vessels ensured equal light exposure at each reaction vessel.

Typical Photolysis Procedure. In a typical photolysis experiment the ketone was dissolved in the appropriate solvent. The solution was placed in the reaction vessel which was held in place around the immersion well apparatus described above. Nitrogen was bubbled through the solution for at least 15 min prior to irradiation. At the end of this period the bubbling was stopped, but a positive pressure of nitrogen was maintained throughout the reaction. Aliquots were periodically withdrawn to ascertain the extent of reaction. Infrared and ultraviolet spectroscopy, together with glpc and tlc (Eastman Chromagram sheets) were some of the methods used for determining the extent of reaction. The reaction was stopped at the appropriate time depending on the nature of the compound and the experiment.

Materials. Enone (**10**) was recrystallized from ethyl acetate–hexane until it had a constant melting point of 79–80° and was pure by glpc analysis. Benzene was distilled through a Vigreux column. The cloudy benzene–water azeotrope was discarded. The fraction boiling at 80–81° was used. Reagent grade toluene (Baker Analyzed), reagent grade *t*-butyl alcohol (Baker Analyzed), spectral grade chloroform, and spectral grade dioxane were used without further purification. Piperylene (Fisher Chemicals) was distilled, bp 42–44°. Benzil was recrystallized from absolute ethanol, mp 95–96°. Acenaphthene was recrystallized from ethanol, mp 93–94°.

10-Carbethoxy-$\Delta^{1,9}$-octalone was prepared from 2-carbethoxycyclohexanone[49,50] (42.5 g, 0.25 mol) in alcoholic sodium ethoxide by reaction with 4-diethylamino-2-butanone methiodide[15] to give 27 g (50%) of the desired compound, bp 125° (0.5 mm).[19]

2-Hydroxy-10-hydroxymethyl-$\Delta^{1,9}$-octalin was prepared by reaction of lithium aluminum hydride (6 g, 0.16 mol) with 10-carbethoxy-$\Delta^{1,9}$-2-octalone (20 g, 0.09 mol) to give 14 g, (70%), mp 115–116° (lit.[14] mp 119–120°).

10-Hydroxymethyl-$\Delta^{1,9}$-2-octalone (10). (4a-Hydroxymethyl-4,4a,5,6,7,8-hexahydro-2(3H)-naphthalenone). Method A. A solution of the diol above (10 g, 0.055 mol) and 2,3-dichloro-5,6-dicyanobenzoquinone (15 g, 0.066 mol) in 200 ml of dioxane was stirred at room temperature for 16 hr. The precipitated quinol was collected and washed with ether. The filtrate and washings were evaporated and the resulting residue was dissolved in ether and washed repeatedly with 10% sodium hydroxide followed by water until neutral. The dried solution was evaporated yielding a white crystalline solid. Recrystallization from ethyl acetate–cyclohexane yielded 5 g (50%), mp 79–80° (lit.[14] mp 78.5–79.5°).

Compound **10** has a carbonyl band at 1670 cm^{-1}, a C=C stretch at 1630 cm^{-1}, and typical OH bands. Its nmr spectrum has singlets at δ 5.80 ppm (vinyl), 4.20 ppm (OH), 3.72 ppm (CH$_2$OH), and a complex absorption from 1.0 to 2.5 ppm. Its chief mass spectral peaks, *m/e* (% of base), are at 180 (25), 151 (14), 150 (100), 149 (22), 122 (33), 121 (29), 108 (16), 107 (52), 105 (15), 93 (31), 91 (57), 79 (59) and 77 (43).

10-Hydroxymethyl-$\Delta^{1,9}$-2-octalone. Method B. The synthesis from 10-carbethoxy-$\Delta^{1,9}$-2-octalone *via* the intermediate dioxolan was carried out substantially as described earlier.[14] The compound isolated was identical with that obtained above by the reduction–oxidation route.

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[47] W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. Carroll, *J. Amer. Chem. Soc.*, **88**, 1199 (1966), and reference cited therein.

[48] J. E. Baldwin and J. A. Kapecki, *ibid.*, **91**, 3106 (1969), and references cited therein.

[49] H. R. Snyder, L. A. Brooks, and S. H. Shapiro, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 531.

[50] G. Stork, A. Brizzolara, H. Landesmann, J. Szmuskovic, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

β-Methoxy-1,2,3,4,5,8-hexahydronaphthalene was prepared from β-methoxy-1,2,3,4-tetrahydronaphthalene[51] by the method of Fassnacht and Nelson.[52] The crude product (12.0 g, 92% yield) was used without further purification.

$\Delta^{1,9}$-2-Octalone (12) was prepared by hydrolysis of the enol ether above.[52] The product (63%) had bp 56–58° (1 mm), had no vinyl H (nmr), and had an ir carbonyl bond at 1710 cm^{-1}.

$\Delta^{1,9}$-2-Octalone (13) and $\Delta^{9,10}$-2-Octalone (12). A mixture of these compounds was prepared exactly as reported by Stork,[50] from cyclohexanone morpholine enamine and methyl vinyl ketone. The mixture contains 72% **13** and 28% **12**.

$\Delta^{1,9}$-2-Octalone (13).[50] The pure conjugated octalone was obtained by cooling a hexane solution of the octalone mixture in Dry Ice–acetone. The conjugated isomer crystallized under these conditions and was filtered with suction through a fritted glass filter. The compound is a liquid at room temperature, bp 89–90° (1 mm) (lit.[50] bp 68–69° (0.1 mm)). There was a vinyl H (nmr) at 5.66 ppm and ir and uv spectra as reported.[50]

2-Hydroxymethyltricyclo[5.3.0.0^{2,7}]decan-10-one (11) (Lumiproduct). Four glass-stoppered Pyrex tubes containing 0.1 g of enone (**10**) in 10 ml of *t*-butyl alcohol were put in positions adjacent to the quartz immersion well described above. After irradiation for 600 hr, glpc analysis indicated the presence of 25% unreacted starting material and 45% product. Each tube was worked up by removing the solvent *in vacuo*. The residue was then taken up in a small amount of acetone and repeated injections of 50 μl were made into an Aerograph Model A-700 gas chromatograph. A 10 ft × 0.25 in. 15% SE-30 on Chromosorb W, A/W DMCS column was used with column temperature 210°, detector 250°, injection port 250°, and helium flow rate 65 ml/min. The peak corresponding to lumiproduct was collected using an "L" tube which passed into an nmr tube. Compound **11** had the following mass spectrum: *m/e* (% of base peak): 180 (15), 150 (89), 135 (15), 133 (15), 122 (41), 121 (33), 109 (52), 108 (30), 107 (68), 105 (34), 95 (29), 91 (89), 79 (100), 77 (66), 67 (64). The nmr spectrum ($CDCl_3$) had a singlet at 3.67 ppm and a complex absorption from 1.0 to 2.7 ppm. The ir spectrum showed a carbonyl band at 1700 cm^{-1} and typical hydroxy absorption, with no bands indicating C=C.

$\Delta^{8,9}$-2-Octalone (14) was prepared by the method of Ringold and Malhotra.[53] A mixture of octalone (**13**) (0.5 g, 0.0033 mol) and potassium *t*-butoxide (3.7 g, 0.033 mol) in *t*-butyl alcohol was stirred under nitrogen for 1.5 hr at room temperature and then quenched by rapid addition of 100 ml of 10% acetic acid to the resulting slurry. Excess aqueous bicarbonate was added and the product isolated by ether extraction, yielding 0.45 g (90%). The compound had a vinyl H (nmr) at 5.38 ppm and a very complex absorption from 1.0 to 3.0 ppm.[19] The ir spectrum showed no OH band, a carbonyl bond at 1715 cm^{-1}, and a C=C band at 1660 cm^{-1}.

Quenching Experiments. In a typical experiment approximately 0.02 g of enone (**10**) was weighed into a 5-ml volumetric flask. The compound was dissolved in the appropriate solvent and 0.5-ml aliquots were withdrawn and placed into the Pyrex sample tubes. The quencher, piperylene, was added with a microsyringe and solvent was added to a total volume of 4 ml. The sample tubes were irradiated using the merry-go-round apparatus described above under conditions such that the enone (**10**) was absorbing all the light. After irradiation for 2 hr, the proper amount of a freshly prepared standard solution (acenaphthene in acetone) was added volumetrically. Some of the solvent was removed in a stream of dry nitrogen. The resulting solutions were analyzed by glpc using the standard technique described. Areas were measured where possible using the Disc chart integrator. In other cases, a compensating planar polarimeter was used.

Sensitization Experiment. In the sensitization experiment three tubes were prepared, each containing 0.026 g of enone (**10**) in 3 ml toluene (4.8 × 10^{-2} *M*). One tube also contained 0.165 g of acetophenone (4.6 × 10^{-1} *M*), another contained 0.250 g of benzophenone (4.6 × 10^{-1} *M*). The total absorbance of each tube was calculated by multiplying the concentration by the extinction coefficient at the major resonance lines of the mercury arc lamp. The acetophenone absorbed over 96% of the light, and the benzophenone absorbed over 92% of the light. The tubes were irradiated using the merry-go-round apparatus and Pyrex filters. As mentioned in the Results, problems with glpc analysis precluded quantitative analysis of this experiment. However, there was more conversion to products in the tubes containing sensitizer than could be accounted for by the enone absorption. Thus, benzophenone, and acetophenone sensitize the reaction. Also, the same products are formed as in the direct irradiation.

Quantum Yield Procedure. The method of Hatchard and Parker[18] was employed, in which potassium ferrioxolate is the actinometer. A Bausch and Lomb Model 33-86-25 ultraviolet grating monochromator equipped with a 200-W super pressure mercury source and power supply was used as the light source. The quantitative determination of enone disappearance was accomplished using benzil as internal standard. Product formation was quantitatively determined using acenaphthene as internal standard weighed into the cell. Benzene was then added. After irradiating for 11.5 hr and treatment as usual,[18] the data in Table II were calculated.

Glpc Coinjection Experiments. The following two columns were used for all coinjection experiments: 6 ft × $^1/_8$ in. 15% SE-30 on Chromosorb W, A/W DMCS treated; 4 ft × $^1/_8$ in. 10% Carbowax 20M on Chromosorb P untreated. It is important to realize that these columns have very different properties. The first is composed of a nonpolar liquid phase on a very unreactive support; the second has a polar liquid phase on a reactive support. The fact that coinjection results were identical on these two columns is strong evidence in favor of the conclusions drawn from these experiments. In addition, many of the nonalcoholic compounds studied were coinjected on a number of other columns including XF-1150, DC-11, and Apiezon L.

Bibenzyl was identified using the two columns mentioned above. Biphenyl was identified by coinjection on the SE-30 column, a 6 ft × $^1/_8$ in. 10% Carbowax 20M on Chromosorb W, A/W DMCS treated column, and a 6 ft × $^1/_8$ in. 4% QF-1, 1% Carbowax 20M on Chromosorb G, A/W DMCS treated column.

Acknowledgments. The authors gratefully acknowledge generous support of this investigation by the U. S. Army Research Office (Durham) through grants under project 4019-C. D. I. S. wishes also to acknowledge stimulating and fruitful discussions with Dr. Kurt Schaffner at the ETH, Zurich, Dr. M. J. Perkins of Kings' College, London, and Professor Jack Saltiel of Florida State University.

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