Further elution of the column with benzene gave 100 mg of 2-phenyl-1,4-napthoquinone (XV), mp 111-112°. The quinone, formed in 10% yield, was characterized by the following spectral properties: ultraviolet spectrum had $\lambda\lambda_{\max}$ (95% ethanol) 337 mμ (ϵ 4600), 303 (6800), and 249 (24,700); infrared spectrum had $\lambda_{\max}$ (KBr) 6.03, 6.30, 13.19, and 14.50 μ; 60-Mc nmr (deuteriochloroform) showed multiplet at τ 2.17 (nine protons), singlet at 2.97 (one proton). Proof of structure XV was obtained by comparison with an authentic sample.[50] Further elution of the chromatographic column with 10% ethyl acetate-benzene gave 300 mg of 3,4-diphenyl-4-hydroxy-2-butenoic (35%) acid γ-lactone (XI), identified by comparison of its infrared spectrum with that of an authentic sample.

Irradiation of 2,3-Diphenylfuran. A solution of 500 mg of 2,3-diphenylfuran[27] in 100 ml of anhydrous benzene was irradiated with an internal, water-cooled mercury arc lamp (Hanovia, Type L, 450 w) with a Vycor filter. Aliquots were removed and analyzed by gas-liquid chromatography. The analytical gas chromatography was performed on an Aerograph Hy-Fi instrument with nitrogen as the carrier gas on a column of SE-30 (5%) on Chromosorb W at 225°. After 20 hr the peak due to starting material had completely disappeared and a new peak appeared with a slightly higher retention time. At no time during the irradiation did any other peak appear. After the irradiation was completed, the solution was evaporated to dryness to give an orange oil. The crude residue was chromatographed on a 3 × 98 cm silica gel column. The column was eluted with 1 l. of benzene. The eluent, in 50-ml fractions, was concentrated and dried *in vacuo*. Fractions 9-14 contained 200 mg of a white solid, mp 112-114°. Recrystallization from pentane and vacuum sublimation at 0.1 mm in a microsublimation apparatus gave crystals, mp 118.5-119°, which gave a satisfactory elemental analysis for [9,10-*b*]phenanthrofuran (XVI).

Anal. Calcd for $C_{16}H_{10}O$: C, 88.05; H, 4.62. Found: C, 87.80; H, 4.85.

The infrared spectrum of this material showed a strong band at 13.1 μ. The ultraviolet spectrum (95% ethanol) has $\lambda\lambda_{\max}$ at 352 mμ (ϵ 1300), 335 (1200), 320 (800), 3.02 (12,300), 290 (10,600), 280 (14,800), 254 (64,600), 249 (52,100), and 237 (30,000). The molecular weight (calcd 218, found 228) is consistent with a monomeric unit. The structure of this material was determined to be [9,10-*b*]phenanthrofuran (XVI) by conversion to [9,10-*b*]phenanthrofuran-2-carboxaldehyde (XVII) and comparison to a sample of XVII independently synthesized as described below.

Preparation of [9,10-*b*]Phenanthro-2-carboxaldehyde (XVII). To 500 mg of dimethylformamide with stirring and cooling in an ice bath was added 142 mg of phosphorus oxytrichloride. The mixture was subsequently stirred for 10 min in the ice bath and then 170 mg of [9,10-*b*]phenanthrofuran (XVI) was added to the cooled solution. The mixture was kept at 0° for 10 min and at 80° for 5 min and then poured onto ice. The aqueous layer was extracted with ether and the extracts were dried over sodium sulfate. Evaporation of the solvent and drying afforded 450 mg of a dark oil. The crude mixture was dissolved in benzene and passed through an alumina column (activity III). Elution of the chromatographic column with 1% ethyl acetate-benzene gave 150 mg of a yellow solid, mp 146-152°. Recrystallization from hexane-benzene gave yellow needles, mp 153-154° dec.

Anal. Calcd for $C_{17}H_{10}O_2$: C, 82.91; H. 4.09. Found: C, 82.79; H, 4.43.

The infrared spectrum of the crystalline compound in a KBr pellet is characterized by a strong band at 5.97 and bands at 8.63, 9.05, 10.52, and 12.31 μ. The ultraviolet spectrum in 95% ethanol has $\lambda\lambda_{\max}$ at 358 mμ (ϵ 12,300), 342 (14,900), 333 (15,500), 257 (40,500), 249 (41,700), and 244 (40,800). The nmr spectrum in deuteriochloroform has a singlet at τ 0.33 (one proton) and two complex multiplets at 1.69 and 2.41 (nine protons). The identity of the Vilsmeier product as [9,10-*b*]phenanthrofuran-2-carboxaldehyde (XVII) was further confirmed by comparison with a sample independently prepared by selenium dioxide oxidation of 2-methyl[9,10-*b*]phenanthrofuran (XVIII).

In a sealed tube was placed 1.0 g of XVIII[39] and 480 mg of selenium dioxide. The tube was heated at 140-150° for 30 min. After the oxidation was complete the contents of the tube were taken up in ether and filtered through a glass funnel to remove selenium metal. Evaporation of the solvent left a dark oil which was chromatographed on a 3 × 48 cm column of silica gel. The column was eluted with 1% ethyl acetate-benzene. After elution of starting material (300 mg) with 800 ml of solvent, 200 mg of a yellow solid was eluted with 750 ml of 2% ethyl acetate-benzene. Recrystallization from hexane afforded yellow needles, mp 152-153°. The infrared and nmr spectra of this material were identical in every detail with that of XVII prepared from the Vilsmeier reaction of XVI. The mixture melting point of these two materials was undepressed at 152-154°.

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(50) A. N. Grinev, A. P. Klyagina, and A. P. Terentev, *Zh. Obshch. Khim.*, **29**, 2773 (1959).

Photosensitized Reactions of Cyclobutene in Solution

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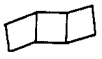
Contribution from the IBM Watson Research Center,
Yorktown Heights, New York. *Received February 7, 1966*

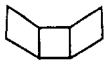
Abstract: Irradiation of a solution of cyclobutene in acetone gives rise to tricyclo[4.2.0.$0^{2,5}$]octane, 5-methyl-4-hexenal, and cyclobutylacetone as the major products. Quantum yields for the formation of these products have been obtained at 2537 and 3130 A as a function of the concentration of cyclobutene. It is believed that 5-methyl-4-hexenal is formed through the addition of an excited acetone molecule to cyclobutene to give an oxetane which subsequently decomposes to this product. The irradiation of acetone and 1-methylcyclobutene gives 6-methyl-5-hepten-2-one in a similar fashion. Cyclobutylacetone is probably formed by a free-radical reaction that is photoinitiated. The formation of all three of the products is quenched by the presence of even a trace of biacetyl. It is estimated that for every collision of a triplet acetone with a cyclobutene that gives an oxetane, there are 11 collisions which result in energy transfer to give a triplet cyclobutene.

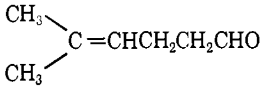
The photochemical reactions that cyclic monoolefins undergo on sensitized excitation have been studied quantitatively in a number of instances in the gas phase, but scarcely ever in solution. In particular, the sensitized reactions of cyclobutene have received very little attention in either phase. The photochemistry of cyclobutene is of interest in two ways: (i) since it is in itself a "small-ring" compound, it can be expected to give novel products through addition reactions, and (ii) the rigidity imposed by the four-membered ring would allow very little freedom to the olefinic group to twist in the excited state. As a result, the range of sensitizer energies which are capable of exciting the molecule will be a narrow one, which in turn may impose a marked wavelength dependence on the photochemistry.

Results

Irradiation of cyclobutene in acetone solution gave rise to three products—one hydrocarbon and two carbonyl compounds. The hydrocarbon which analyzed for C_8H_{12} (molecular weight by mass spectrometry = 108) showed no unsaturation in its infrared or nmr spectrum; hence, it must be a tricyclic. There was no evidence for the presence of a cyclopropane ring in the compound. Since the formula corresponded to a dimer of cyclobutene, it was logical to expect that the compound would be one of the isomers of tricyclo[4.2.0.$0^{2,5}$]-octane.[1] By comparison of the infrared spectrum and the retention time with those of an authentic sample,[2] the dimer was identified as the *anti* isomer (I). Careful search for the *syn* isomer (II) did not lead to a conclusive result. An upper limit of 5% can be placed on its yield relative to that of the *anti* isomer.

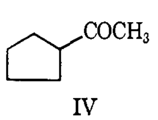

I

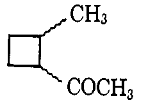

II

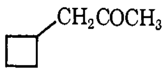

$$(CH_3)_2C{=}CHCH_2CH_2CHO$$
III

Both carbonyl compounds had a molecular formula of $C_7H_{12}O$ which corresponds to a 1:1 adduct of acetone and cyclobutene. One of these was an aldehyde (infrared absorptions at 1740 and 2710 cm^{-1}) which also contained methyl groups (1360 cm^{-1}). The nmr spectrum confirmed the presence of the aldehydic group (one proton at τ 0.29). It also indicated absorptions due to one olefinic proton (*ca.* τ 5), six protons at τ 8.35 (unsplit), and four protons in a broad band centered at 7.7. The structure 5-methyl-4-hexenal (III) would agree with all of these observations.

The second carbonyl compound was a ketone which showed no unsaturation in its spectra. The presence of a CH_3CO group was indicated by an infrared absorption at 1356 cm^{-1} and an intense peak at *m/e* 43 in the mass spectrum. The nmr spectrum showed an absorption at τ 7.95 (unsplit) which was assigned to the protons on this methyl group. The formula demands that the molecule have one ring in it. Since all of the absorptions due to the protons in the nmr spectrum were between τ 7.4 and 8.6, the possibilities seemed to be limited to a cyclobutane or a cyclopentane ring. On repeatedly refluxing the ketone with an excess of deuterium oxide in the presence of a trace of potassium carbonate, it was possible to obtain a deuterated ketone which corresponded to the molecular formula $C_7H_7D_5O$. In its infrared spectrum the methyl absorption at 1356 cm^{-1} as well as the absorption at 1407 cm^{-1}, which can be attributed to a CH_2CO group[3] of the normal ketone, were both absent. These observations eliminated possible structures such as IV and V and showed that the compound had the structure cyclobutylacetone (VI).

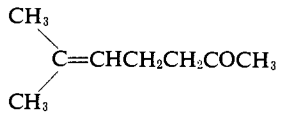

IV


V


VI

The relative yields of these products was a function of the concentration of cyclobutene as well as the wavelength of light that was used. The data that were obtained are summarized in Table I.

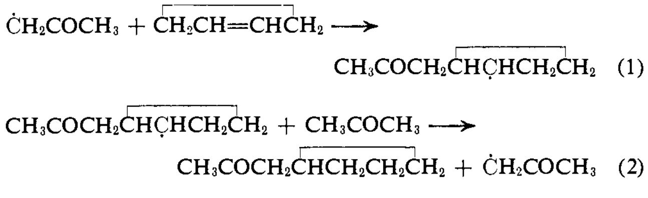
In one experiment, a solution of 1-methylcyclobutene in acetone was irradiated at 2537 A. In the work-up of the solution, only the carbonyl compounds were separated. The major product was an unsaturated ketone which was identified as 6-methyl-5-hepten-2-one (VII) by comparison of its infrared spectrum and retention time with those of an authentic sample, comparing the melting point of its 2,4-dinitrophenylhydrazine derivative with that of the authentic material, and also observing the mixture melting point.


$$(CH_3)_2C{=}CHCH_2CH_2COCH_3$$
VI

Discussion

The mechanisms of the formation of the products reported here call for little comment, as these reactions are well known. The dimerization of cyclobutene is analogous to the ketone-sensitized dimerizations of cyclohexene[4] and norbornene.[5a] These reactions also show a considerable degree of stereospecificity.

The formation of cyclobutylacetone is most probably a free-radical reaction which may involve a chain if it proceeds through the sequence


$$\dot{C}H_2COCH_3 + CH_2CH{=}CHCH_2 \longrightarrow CH_3COCH_2CH\dot{C}HCH_2CH_2 \quad (1)$$

$$CH_3COCH_2CH\dot{C}HCH_2CH_2 + CH_3COCH_3 \longrightarrow CH_3COCH_2CHCH_2CH_2CH_2 + \dot{C}H_2COCH_3 \quad (2)$$

The reaction may be initiated by an excited state of acetone which can be quenched by biacetyl, as shown by the results in Table I. The free-radical character of the reaction is indicated by the quenching action on the reaction of an increase in the concentration of cyclobutene. At concentrations of cyclobutene in excess of 0.36 *M* (at which point the yield of cyclobutylacetone is a maximum), the yield of the product is inversely dependent on the concentration of cyclobutene up to about 0.9 *M*. At higher concentrations of cyclobutene, the yield of cyclobutylacetone falls off even more steeply and is barely detectable in 2 *M* solution. The reaction is entirely similar to the photochemical addition of acetone to norbornene.[5b]

The formation of 5-methyl-4-hexenal is probably *via* the well-known photochemical addition reaction of ketones to olefins. Thus the reaction would initially give the product VIII which decomposes either sponta-

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(1) M. Avram, I. G. Dinulescu, E. Marica, G. Mateesen, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, 97, 382 (1964).

(2) The authors wish to thank Professor C. D. Nenitzescu for samples of the two tricyclooctanes.

(3) R. N. Jones and C. Sandorfy in "Chemical Applications of Spectroscopy," Vol. IX, W. West, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 499.

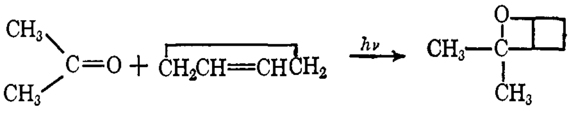
(4) D. R. Arnold, private communication.

(5) (a) D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963); D. R. Arnold, D. W. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, 87, 2596 (1965); (b) W. Reusch, *J. Org. Chem.*, 27, 1882 (1962).

Table I. Irradiation of Solutions of Cyclobutene in Acetone

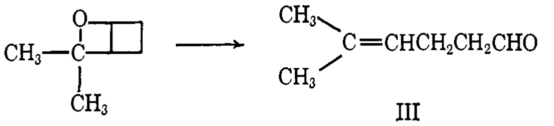
Cyclobutene concn, *M*	Time, min	Quantum yields: Dimer I	Quantum yields: Aldehyde III	Quantum yields: Ketone VI	Remarks
			2537 A		
0.035	150	0.00	0.00	0.007	
0.21	150	0.002	0.00	0.072	$\alpha^a = 21$
0.27	180	0.005	0.002	0.080	$\alpha = 13$
0.36	180	0.006	0.003	0.084	$\alpha = 21$
0.52	180	0.016	0.004	0.067	$\alpha = 17$
0.91	180	0.028	0.006(?)	0.050(?)	$\alpha = 29$
1.76	360	0.052	0.038	0.002	$\alpha = 60$
2.87	360	0.087	0.049	0.0	
2.85	180	0.0	0.0	0.0	Biacetyl = 0.12 *M*
2.81	320	0.0	0.0	0.0	Biacetyl = 0.55 *M*
3.94	360	0.108	0.055	0.0	
			3130 A		
0.28	360	0.002	0.0	0.307	
0.56	180	0.012	0.0	0.171	
2.89	720	0.037	0.004	0.0	

[a] $\alpha = [\text{cyclobutene}]^2/\Phi_{\text{dimer}}$.

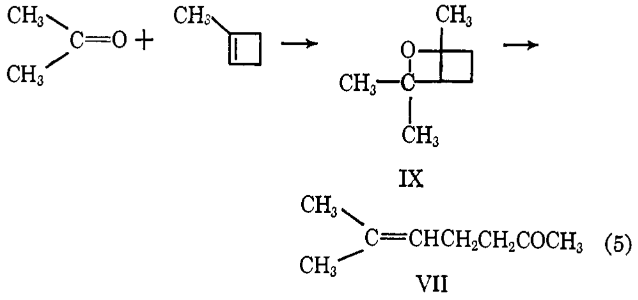


VIII (3)

neously, or during the work-up, to III. It is known[6] that an oxetane such as VIII would pyrolyze preferentially to an unsaturated carbonyl compound rather than by the reverse of reaction 3. Supporting evidence for this mechanism is provided by the reaction between acetone and 1-methylcyclobutene which by a mechanism analogous to reactions 3 and 4 should, and does, give 6-methyl-5-hepten-2-one.



III (4)



IX

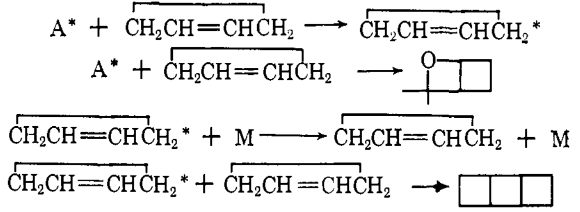
VII (5)

While numerous examples of photochemical systems in which the sensitized dimerization of an olefin or the formation of an oxetane are known, cases in which both reactions occur side by side are few in number. Mention may be made of the system acetone–fumaronitrile[4,7] in which geometric isomerization of the olefin competes with oxetane formation, and benzophenone–2,3-dimethyl-1,3-butadiene in which it has been claimed[8] that both dimerization and oxetane formation occur by the addition of the triplet diene to another diene and ketone molecule, respectively. Kinetic studies have not been reported on any of these systems.

In order to explain the kinetics of the reactions that were observed (excluding the formation of cyclobutylacetone) the following mechanism is proposed.

$$A + h\nu \longrightarrow A^* \qquad (6)$$

$$A^* + M \longrightarrow A + M \qquad (7)$$



A = acetone; M = any molecule in the system

Reaction 6 is meant to include not only the initial excitation to the singlet state of acetone, but also the triplet state that is formed by subsequent crossover. Actually, the reactions reported here probably take place from only the triplet state of acetone, as the addition of only 0.1 *M* of biacetyl to a solution of 2.8 *M* cyclobutene completely quenches the formation of all of the products. The efficient and specific quenching action of biacetyl toward the triplet state of acetone has been well documented in numerous publications.[9a]

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(6) R. Srinivasan and W. Hauser, unpublished results on 1-methyl-2-oxabicyclo[2.2.0]hexane.

(7) J. J. Beereboom and M. Schach von Wittenau, *J. Org. Chem.*, **30**, 1231 (1965).

(8) W. G. Dauben, Preprints of paper presented at Solvay Conference on Organic Photochemistry, Brussels, Oct 1965.

(9) (a) J. Heicklen and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **81**, 3858 (1959), and earlier references therein. (b) A referee has pointed out that eq 15 and 17 require that plots of $1/\Phi_{\text{oxetane}}$ *vs.* 1/[cyclobutene] and $\Phi_{\text{oxetane}}/\Phi_{\text{dimer}}$ *vs.* 1/[cyclobutene] be linear, but the data in Table I do not agree with either equation. He has further suggested that this may indicate a failure of the entire analysis as it is given in eq 12 through 15. It is certainly true that $1/\Phi_{\text{oxetane}}$ does not show a linear relationship to 1/[cyclobutene] over the entire concentration range that is given in Table I, but this may be attributed wholly to the inaccuracy in the oxetane data. It is an inherent problem in this system that the oxetane is never a dominant product. As a result, only in a narrow intermediate range of concentration has it been possible to determine its quantum yield with reasonable accuracy. It has been determined that the absolute quantum yields for the dimer are accurate to ±15% except in very dilute solution and reproducible to ±2%. They are more reliable than the quantum yields for the oxetane at all concentrations by a factor of 3. It is therefore felt that the kinetic analysis of the formation of the dimer (eq 6 through 11 with the exception of 9) can stand on its own. (c) This value is arrived at by taking the ground singlet → *vertical* triplet energy in ethylene, subtracting 5 kcal/mole for disubstitution and 15 kcal/mole for relief of the strain due to a double bond in a cyclobutane ring.

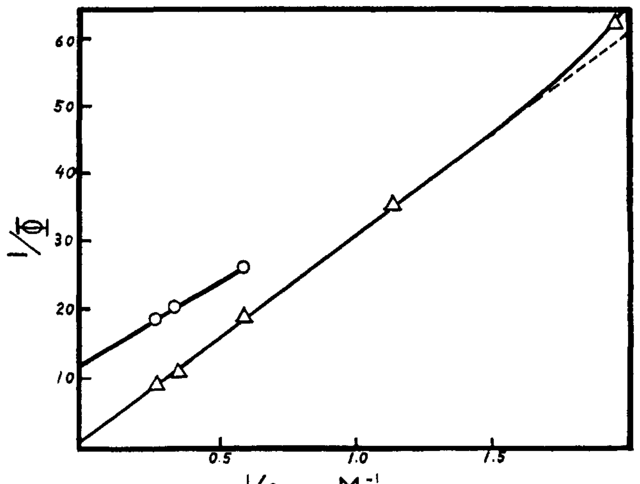

Figure 1. Reciprocal of quantum yields for photoproducts *vs.* reciprocal of cyclobutene concentration: open circles, 5-methyl-4-hexenal; open triangles, tricyclooctane.

From eq 6 through 11, by making the usual stationary state assumptions, it can be derived that

$$\Phi_{\text{dimer}} = k_8k_{11}[\text{cyclobutene}]^2/(k_{10}M + k_{11}[\text{cyclobutene}](k_7M + (k_8 + k_9)[\text{cyclobutene}]) \quad (12)$$

$$\Phi_{\text{oxetane}} = k_0[\text{cyclobutene}]/(k_7M + (k_8 + k_9)[\text{cyclobutene}]) \quad (13)$$

In order to test eq 12 it is best to rearrange it in the form

$$1/\Phi_{\text{dimer}} = \frac{k_8 + k_9}{k_8} + \frac{((k_8 + k_9)k_{10} + k_7k_{11})M}{k_8k_{11}[\text{cyclobutene}]} + \frac{k_7k_{10}}{k_8k_{11}}\frac{M^2}{[\text{cyclobutene}]^2} \quad (14)$$

At low concentrations of cyclobutene, the last term which involves 1/[cyclobutene]^2 would be the most significant, and the dependance of $1/\Phi_{\text{dimer}}$ on 1/[cyclobutene]^2 would represent a parabola. In Table I, the values of [cyclobutene]$^2/\Phi_{\text{dimer}}$ in the concentration range from 0.21 to 0.91 are seen to be reasonably constant. At high concentrations of cyclobutene, the last term can be dropped in comparison with the first two. Then $1/\Phi_{\text{dimer}}$ would show a linear dependance on 1/[cyclobutene]. This is demonstrated in Figure 1. The limiting value of $1/\Phi_{\text{dimer}}$ is $1 + k_9/k_8$ which is experimentally found to be 1.0 ± 0.2. It points out that at sufficiently high concentrations of cyclobutene, both the transfer of triplet energy to cyclobutene and its subsequent addition to another cyclobutene molecule are highly efficient processes.

Equation 13 can be rearranged to give

$$1/\Phi_{\text{oxetane}} = \frac{k_8 + k_9}{k_9} + \frac{k_7M}{k_9[\text{cyclobutene}]} \quad (15)$$

in order to show that $1/\Phi_{\text{oxetane}}$ is a linear function of 1/[cyclobutene]. The values for the quantum yield of oxetane from Table I when plotted against 1/[cyclobutene] fit a straight line rather poorly. This is attributed to the experimental difficulty in determining low quantum yields of the aldehyde derived from the oxetane, especially in the presence of a considerable excess of cyclobutylacetone. However, the values at the three high concentrations of cyclobutene do fit a straight line (Figure 1), which can be extrapolated to give an intercept of 12 for the value of $1/\Phi_{\text{oxetane}}$ at infinite concentration of cyclobutene. Since this is also the value of $1 + k_8/k_9$, $k_8 = 11k_9$. It means that during a collision between a triplet acetone molecule and a cyclobutene, energy transfer is 11 times as likely as oxetane formation. Since both processes involve the same groups in the two molecules, this is a somewhat puzzling result. It can only be interpreted as a fairly strict stereochemical requirement for oxetane formation.

Several interesting aspects of the mechanism proposed here may be pointed out.

(i) Exclusion of reaction 7 will make Φ_{oxetane} independent of [cyclobutene], which would be at variance with experiment.

(ii) If oxetane formation is by

$$\overline{\mathrm{CH_2CH{=}CHCH_2}}^* + \mathrm{A} \longrightarrow \text{oxetane} \quad (16)$$

the Φ_{oxetane} would be inversely proportional to [cyclobutene]. This is really the only test of whether oxetane formation is by reaction 16 or by reaction 9. It has been argued[8] that in the reaction of benzophenone with conjugated dienes, the observation that there is more oxetane formed at low concentration than at high concentration of a diene is evidence in favor of reaction 16.

From eq 14 and 15

$$\Phi_{\text{oxetane}}/\Phi_{\text{dimer}} = \frac{k_9k_{10}M}{k_8k_{11}[\text{cyclobutene}]} + \frac{k_9}{k_8} \quad (17)$$

Evidently, even if oxetane formation is by reaction 9, there can be more oxetane *relative to dimer* at low concentration of olefin than at high concentrations.[9b]

(iii) It is fairly obvious that unless transfer of triplet energy from the ketone to the olefin is totally excluded, there is little point in determining the quantum yield for oxetane formation at just one concentration of olefin as has been reported in the literature.

The relative quantum yields at 3130 A show that the mechanism at this wavelength is not different from that at 2537 A. The surprising feature is the decrease in the absolute values at any given concentration of cyclobutene in going from 2537 to 3130 A. Caution must be exercised in accepting these values, since there is considerable difficulty in measuring quantum yields which are of the order of only a few per cent. However, even after correcting for the differences in the absorption profiles of the reactant (acetone) and the actinometric solution (uranyl oxalate), there is no doubt that the quantum yield for dimerization is smaller at 3130 than at 2537 A. This would mean that either the transfer of energy to the olefin (reaction 8) or the dimerization (reaction 11) (or both) is less efficient at 3130 A. The lowest triplet state of acetone is at 70–73 kcal/mole. If the triplet of cyclobutene is 87 kcal/mole above the ground state,[9c] triplet acetone in its lowest vibrational state would be an inefficient sensitizer. The twisting of the triplet cyclobutene would tend to decrease the endothermicity of its formation, but a significant degree of twist (without opening of the ring) is hard to conceive.[10] One solution seems

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[10] Since 1,3-butadiene is not a product of the sensitization process in solution, an open structure such as $\cdot CH_2CH{=}CHCH_2\cdot$ for the triplet of cyclobutene seems unlikely.

to be to assume that triplet acetone retains some vibrational excitation when it sensitizes the cyclobutene, although it is assumed that such "hot" molecules come into thermal equilibrium with the surrounding in about 10^{-12} sec. Further experiments to clarify these points are being undertaken.

Experimental Section

Cyclobutene was prepared by the photoisomerization of 1,3-butadiene. The experimental sample was at least 99.4% pure. The only impurity was bicyclo[1.1.0]butane. Butadiene was undetectable in the sample, either before or after the photosensitized reaction. Acetone (Eastman Kodak Spectrograde) was used as obtained.

Irradiations were carried out in cylindrical quartz or Pyrex tubes, 1 cm in diameter. The surface of the tube above the liquid level was covered with black tape to eliminate reactions in the vapor phase. The light source was a bank of 16 low-pressure mercury resonance lamps arranged in a circle around the cell, or 16 fluorescent lamps with their emission peaked at 3130 A arranged similarly.[11] Absorbed intensities were 1.09×10^{18} quanta/ml/min at 2537 A, and 3.24×10^{17} quanta/ml/min at 3130 A. The light sources were calibrated with a uranyl oxalate actinometer.

In quantitative studies, a measured quantity (1 to 4 ml) of acetone was added to the cell, which was then attached to a vacuum line and degassed. The cyclobutene which was stored as a gas sample on the line was measured volumetrically and condensed into the same cell. The cell was sealed and detached from the line. Condensation of a significant quantity of mercury was avoided. At the end of the irradiation the cell was cooled and cut open, and the contents was analyzed by vapor phase chromatography.

Preparation of Cyclobutylacetone. A solution of cyclobutene (100 ml, 0.25 *M*) in acetone was irradiated at 3130 A at an intensity of 10^{18} quanta/ml/min for 36 hr. The solution was worked up by distillation followed by vapor phase chromatography to give 1.2 g of cyclobutylacetone (60%), bp 154°, $n^{24.5}\text{D}$ 1.4328; 2,4-dinitrophenylhydrazone had mp 133.0 (Kofler hot stage (lit.[12] mp 131–133°).

Preparation of I and III. A solution (30 ml, 4 *M*) of cyclobutene in acetone was irradiated in a Rayonet reactor[11] for 24 hr. The reaction was stopped and the unreacted acetone and cyclobutene were recovered by distillation. The residue was separated by vapor phase chromatography (2-m Ucon oil column 100°) into (i) 1.0 g (35%), and (III) 0.25 g (10%).

5-Methyl-4-hexenal 2,4-dinitrophenylhydrazone had mp 133 (lit.[13] mp 133°).

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(11) Supplied by the Southern New England Ultraviolet Co., Middletown, Conn.

(12) A. Burger, R. T. Scandridge, N. E. Stjernstrom, and P. Marchini, *J. Med. Pharm. Chem.*, 4, 517 (1961).

(13) A. Lauchenauer and H. Schinz, *Helv. Chim. Acta*, 32, 1265 (1949).

Photolyses of Phenylketene Acetals

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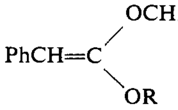
Abstract: Eight phenylketene dialkyl acetals have been photolyzed in cyclohexane and found to give a diversity of products: alkenes, alkylphenylacetates, phenylalkylacetates, phenylcyclohexylacetates, *o*-alkylphenylacetates, and photodimers.

Phenylketene acetals (**1**, **2**, and **3**) offer an attractive subject for photochemical study; their photochemical behavior might be expected to show informative correspondences with three unrelated processes: thermal decompositions of phenylketene acetals, thermal or photolytic decompositions of aryl and vinyl ethers and esters, and photodimerization of styrenes. The photochemistry of eight phenylketene acetals (**1**, **2**, and **3**), prepared by dehydrobromination of the corresponding α-bromophenylacetaldehyde acetals,[2] has been investigated in this initial survey.

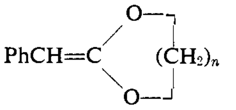
$PhCH{=}C(OR)_2$

1a, R = Me
b, R = Et
c, R = *n*-Pr
d, R = *i*-Pr



$PhCH{=}C(OCH_3)(OR)$

2a, R = Et
b, R = *sec*-Bu



3a, *n* = 3
b, *n* = 2

Results

Identifications of the products obtained through photochemical decompositions of phenylketene acetals were accomplished through spectroscopic methods and comparisons with known compounds. We first summarize the products derived photolytically from **1**, **2**, and **3** and control experiments demonstrating that they are primary photoproducts, then describe syntheses of needed reference compounds.

Photoproducts from Phenylketene Acetals. The structures of the major photoproducts from photolyses of phenylketene acetals in cyclohexane were demonstrated principally by their nmr spectra. The other spectral and physical properties determined for these compounds were in agreement with the assigned structures. Structures of the minor products were assigned mainly from their vpc retention times and infrared spectral comparisons with authentic materials. Certain nmr peaks attributable to some of the minor products could be seen and assigned in spectra obtained for the photomixture or for enriched distillation fractions.

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(1) National Science Foundation Cooperative Graduate Fellow, 1963–1966.

(2) J. E. Baldwin and L. E. Walker, to be published.