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THE PHOTOCHEMISTRY OF CYCLIC NONENOLIZABLE α-DIKETONES AND KETONES INFLUENCE OF REMOTELY POSITIONED SULFIDE, SULFONE, AND SULFOXIDE FUNCTIONALITIES[1]

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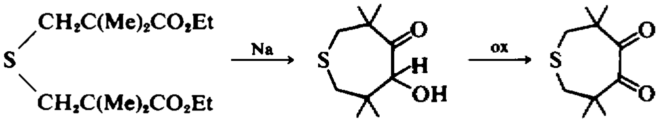
Abstract—The photochemistry of 3,3,6,6-tetramethyl-1-thiacycloheptane-4,5-dione has been examined along with that of the corresponding S-oxide and S,S-dioxide. The chief photochemical process in the first mentioned compound is ring contraction affording 3,3-dimethyl-1-thia-cyclobutan-2-one, isobutene, and carbon monoxide. In addition a small amount of 3,3,6,6-tetramethyl-1-thiacyclohexan-4-one is formed along with two isomeric unsaturated aldehydes. On independent irradiation this thiacyclohexanone affords the same products as its 7-membered diketone counterpart. Similar products are obtained for the S-dioxides investigated save that the ring contraction process was absent. The S-oxides gave no identifiable products. All the results are rationalized in terms of a generalized mechanism involving biradical intermediates.

INTRODUCTION

Research on the cyclic diketone 1 (Eq 1) has opened the way to a variety of *ortho*-di-t-butylheteroaromatics[2] as well as strained alkenes.[3] Other workers have also profited from 1.[4] These intermediates, so useful for synthetic ends, awakened our longstanding interest in photochemistry.[5]



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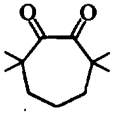
Two questions especially intrigued us. First, will the sulfide linkage in 1 induce large discrepancies in behaviour from that of saturated analog 2? There is good precedent for suspecting that this could be the case.[6] Second, examination of models indicates that 1a, with an approximately orthogonal arrangements of the CO groups, is a favored conformation.[7] To what extent will this influence the photochemistry of the α-dicarbonyl system?



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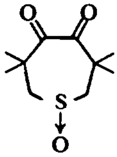

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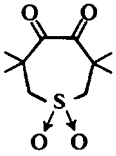

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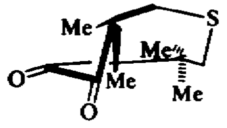
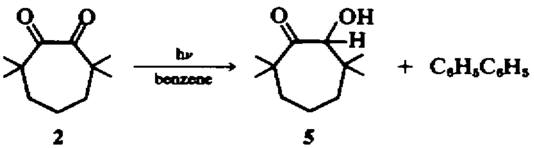


1a

We report here the photochemical reactions of 1, associated model systems 2–4, and the photochemistry of some products derived from 1–4.

RESULTS

Orientational work was carried out with dione 2. On irradiation in benzene solution using a high pressure mercury lamp in a quartz apparatus, sluggish reduction to 5 occurred (Eq 2). This type of reaction is common to other cyclic, nonenolizable diketones, the exact means by which H atoms are obtained being uncertain.[8] However, the anticipation that 1 would deviate sharply from 2 in photochemical behaviour was well fulfilled. When irra-



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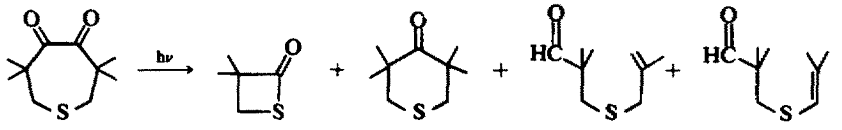


1 **6** (19%) **7** (1%) **8** (1%) **9** (1%)

$+ (Me)_2C{=}CH_2$ (37%) + CO (yield not det'n) (3)

diated under the same conditions as for **2** the products shown in Eq 3 were obtained. The chief product was β-thio-lactone, **6**, which was identified by comparison of spectra with those of an authentic sample.[9] The yield of **6** is that at 35% consumption of **1**; **6** is photochemically unstable leading to its extensive destruction. The second major product is isobutene; the indicated yield is a minimum. All attempts to demonstrate the presence of 2,2-dimethylcyclopropanone met with failure (this could conceivably be the precursor of isobutene and CO) although the cyclopropanone was shown to be stable under the irradiation conditions. Compounds **7–9** formed in trace amounts were isolated by preparative GLPC. Ketone **7** is a known compound[3b] and **8** and **9** were identified by their spectra (Experimental).

The same product distribution was obtained using 250, 300 and 350 nm lamp sources (Rayonet photochemical reactor) using benzene, methanol, or cyclohexane as the solvent. At 250 nm in benzene the reaction was appreciably slower probably due to competitive light absorption by the solvent. There was no evidence that benzene sensitizes the reaction.

Especially interesting was the observation that γ-ketosulfide **7** afforded on irradiation the *same* products as **1** (Eq 4). Conversion to products occurs as fast or faster than with **2**. Could this mean that the reaction sequence is decarbonylation of **1**

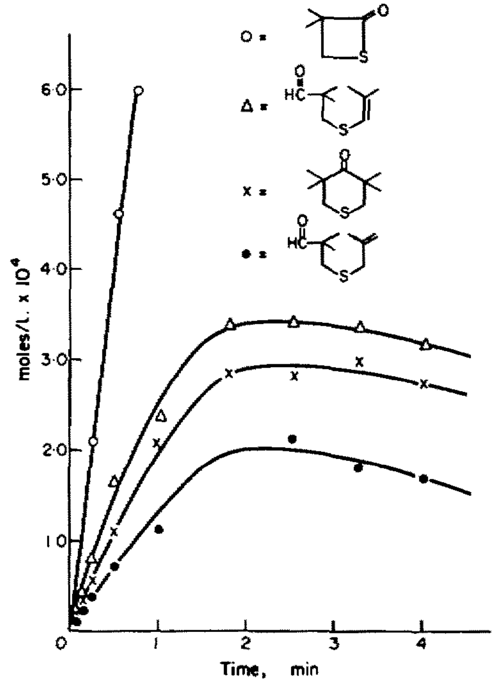
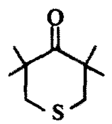


Fig 1. Product formation from **1** (not shown in Fig, starting concentration $25 \cdot 10^{-2}$ M). The yield of **6** rises to a maximum at about 4 hr. Irradiation was carried out at 254 nm in degassed benzene solution.



$$\xrightarrow{h\nu} 6\,(57\%) + 8\,(7\%) + 9\,(1\%) + \underbrace{(Me)_2C{=}CH_2 + CO}_{\text{(yield not det'n)}} \quad (4)$$

yielding **7**, which is the true precursor of the other products? Two lines of argument can be advanced against this possibility. First, as shown in Fig 1, products **6–9** are formed at nearly equal rates beginning from zero time; after about an hour decomposition becomes serious. There is no initial build up of **7**, followed later by the other products. Second, **1** gives products at 350 nm whereas **7** does not even absorb light at this wavelength (λ_{max} 302 nm, ε 31). The relative rates of formation of products from **7** is shown in Fig 2.

To obtain insight into the function of the S atom in **1**, the sulfone **4** was prepared by oxidation of **1** with *m*-chloroperbenzoic acid. Irradiation afforded the products shown in Eq 5. The γ-keto-sulfone **10** was identified by comparison with an authentic sample prepared by oxidation of **7**. The unsaturated aldehydes **11** and **12** were isolated by preparative GLPC and were identified by their spectral characteristics. There is a good possibility that a portion of **12** isomerized to **11** during the tedious isolation process. Isobutene was not detected. Irradiation at 250, 300, and 350 nm in benzene, cyclohexane, and methanol afforded the same products. However in the latter solvent the rate of disappearance was appreciably lower. The γ-

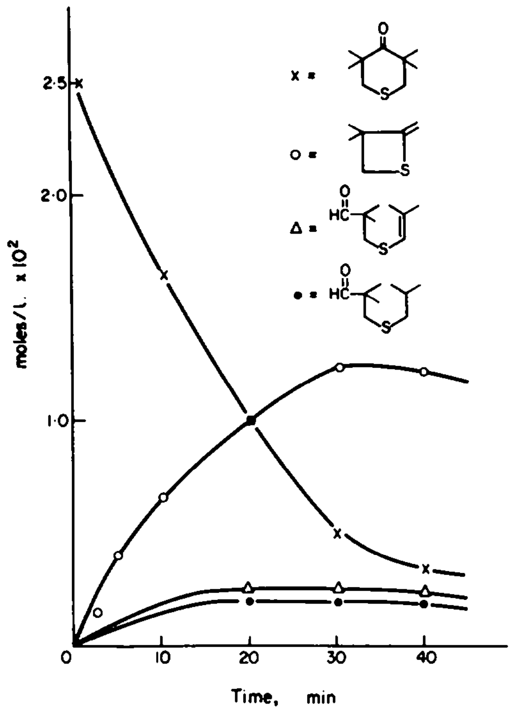
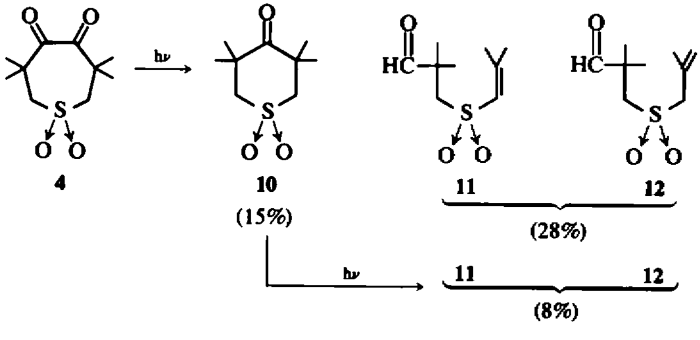


Fig 2. Decomposition of 7 as function of time. Irradiation was in degassed benzene solution at 254 nm.



(5)

ketosulfone **10** yielded only a small amount of **11** and **12** on irradiation and no other identifiable products (Eq 5).

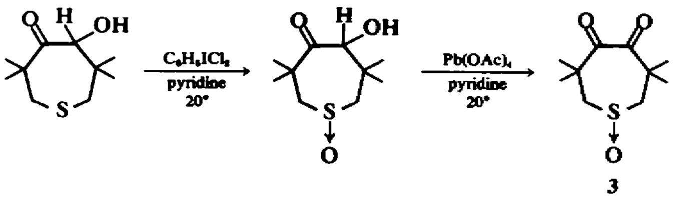
After considerable experimental difficulty a synthesis of the sulfoxide **3** was developed. Reagents normally used to oxidize the S atom led to sulfide-sulfone mixtures. Even the selective reagent, $NaIO_4$,[10] gave only low yields of sulfone. By the route shown in Eq 6 pure **3** was finally obtained. However the expended effort was not rewarded. On irradiation, **3** ungraciously gave only intractable tars.

DISCUSSION

Of the various possibilities, we suggest that the generalized scheme shown in Eq 7 best accounts for the observed photochemical results with **1** and its 6-membered counterpart **7**. The central intermediate is biradical **13** formed from either **1** or **7** (but from the latter only at shorter wavelengths). Biradical **13** undergoes the anticipated reaction, namely β-elimination of a thiyl radical.[11] The products are isobutene and β-thio-lactone **6**. (Radical attack on sulfur followed by loss of isobutene gives the same product). Biradical **13** likewise couples to afford **7** or disproportionates to give **8** and **9**.

The scheme given in Eq 7 can readily be extended to the sulfones **4** and **10**. In this case β-scission of an intermediate biradical analogous to **13** (S replaced by SO_2) is expected to be much less facile since a sulfonyl rather than a thiyl radical must be eliminated.

After competition of the experimental portion of this paper, a report appeared describing the photochemical behaviour of **1** and **7** in fluorocarbon and hydroxylic solvents.[12] Except for some yield differences and the trapping of some dimethyl ketene (from photochemical decomposition of **1**) in alcoholic solvent, there is excellent correspondence with our observations. In this case, however, a mechanistic interpretation was offered involving several competing pathways. Norrish Type I and Type II reactions were suggested to account for



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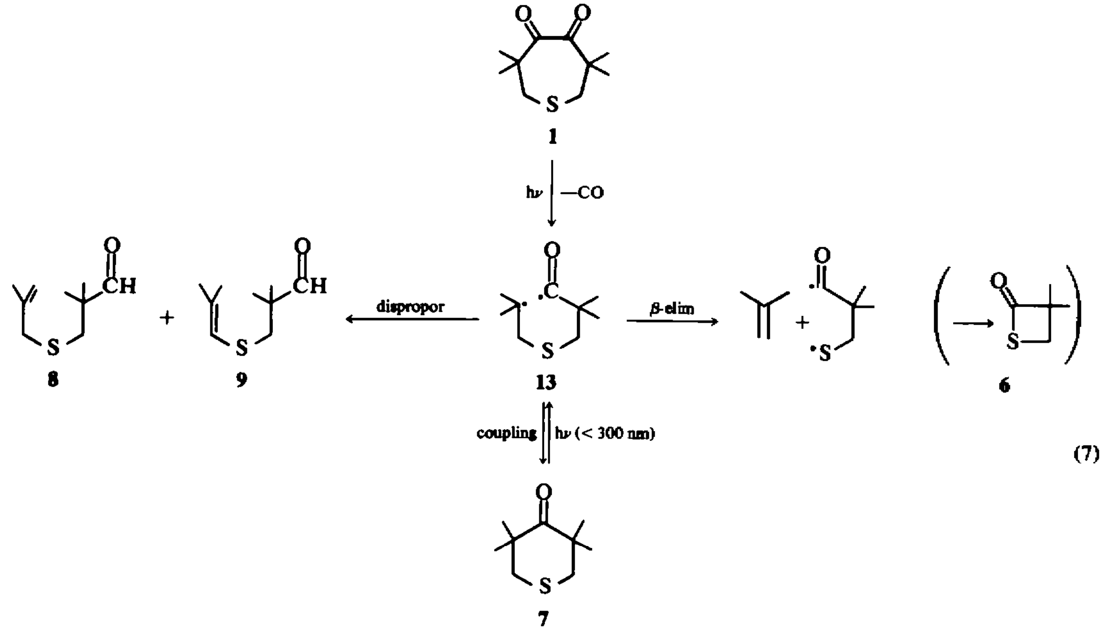
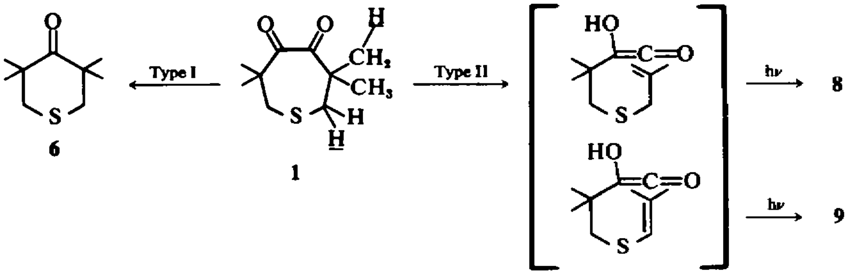


(7)

respectively **6** and for **8** and **9** (Eq 8). The chief pathway was assumed to involve sulfur-carbonyl bonding *via* "charge-transfer interaction" as depicted in Eq 9.* Conceivable modes of decomposition of **14** are path "a" (given in Ref 12) or "path b" involving direct formation of **6** and (probably) cyclopropanone (the presence of which could not be demonstrated).



(8)

These interpretations suffer from the following defects in our opinion. First, the formation of appreciable yields of unsaturated aldehydes from 6-membered rings **7** and **10** indicates that a path exists not involving Norrish Type II reactions for the simple reason that the needed 6-membered transition state is unattainable in these compounds. However the very low yields of unsaturated aldehydes from especially **1** make this point rather academic. More importantly, the strong correspondence in photochemical behavior of sulfide **1** and sulfone **4** as contrasted to methylene analog **2** are indicative of common intermediates. Direct CO-S interaction is highly unlikely in sulfone **4**, yet there is correspondence in behaviour with **1**, resulting *ipso facto* in a lessened probability of such interaction in **1**. Moreover, for obvious steric reasons transannular interactions are more common in medium sized rings (8- to 11-membered)[14] yet a "charge-transfer" interpretation would require equally good interaction in both 7-membered ring **1** and 6-membered ring **7**, which also exhibits the same ring-contraction.† The ultimate validity of the scheme proposed here can only be demonstrat-

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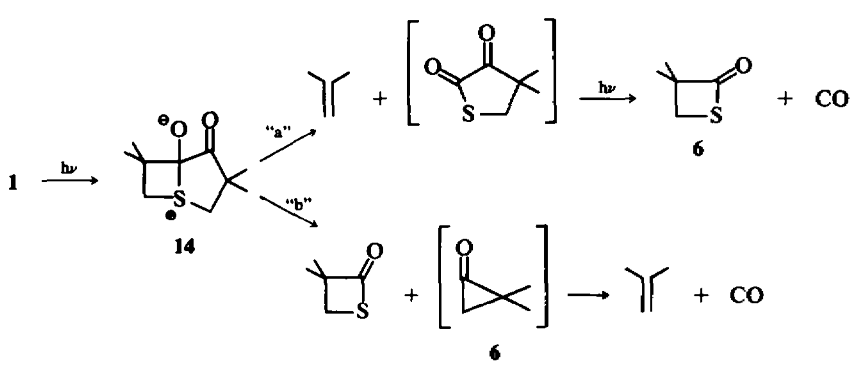
*The term "charge-transfer interaction" is rather loosely used in the literature to describe either an electron abstraction process or formation of a true chemical bond between a CO group and sulfur as indicated in **14** (see, for example, Ref **6e**). This terminology is quite misleading as the chemical processes leading to ultimate bonding need not involve the actual phenomenon of intramolecular charge-traesfer interaction as defined in the sense expressed by Mulliken.[13]

†But electron abstraction from sulfides by excited CO groups does occur in intermolecular reactions. See, for example, [a]J. Gutternplan and S. G. Cohen, *Chem. Commun.* 247 (1969); [b]R. G. Zepp and P. J. Wagner, *Ibid.* 167 (1972)



(9)

ed by detailed mechanistic work. However, at this stage of knowledge, it provides a flexible and general rationalization of the effect of remotely positioned sulfide and sulfone groups in the systems studied here.

EXPERIMENTAL

M.ps were determined on a calibrated m.p. block, b.ps are uncorrected. All spectra were obtained using standard laboratory instruments. Products from various photochemical reactions were isolated using F & M 700 instruments equipped with thermal conductivity detectors. Most preparative scale reactions were carried out in solution using a Hanau TQ-81 medium pressure mercury lamp enclosed in Vycor glass. Yields were improved considerably in later runs using an apparatus consisting of a water cooled TQ-81 lamp around which a large Soxhlet thimble was arranged. The Soxhlet thimble was connected to a large pot of refluxing ether (protected from UV light). A dropping funnel with a Teflon screw device to regulate flow was used to feed substrate into the Soxhlet thimble. Within 3-4 min the thimble had filled and drained into the receiving pot removing the photoproducts from further irradiation. By adjusting the addition rate from the dropping funnel and the reflux rate, high conversion with lower product destruction could be obtained.

The method[2] developed in laboratory was used for the synthesis of 1. Other materials mentioned without reference were prepared by common laboratory procedures.

Microanalyses were performed in the analytical section of this University under the direction of Mr. W. Hazenberg.

3,3,6,6-Tetramethyl-1-thiacycloheptane-4,5-dione-1,1-dioxide (4) was prepared by allowing 1 (600 mg, 2 mmole) dissolved in 50 ml chloroform to react with *m*-chloroperbenzoic acid (10 g, 5 mmole active peroxide). After standing overnight the *m*-chlorobenzoic acid was filtered off and the chloroform soln was washed with water and dried over $MgSO_4$. Chromatography over neutral alumina provided 480 mg (72%) of 4, m.p. 186–187·5°, after recrystallization from MeOH, uv(EtOH) 330 nm (ε 29) and 302 nm (ε 37); NMR ($CDCl_3$) δ 1·42 (s, 12, Me) and δ 3·23 (s, 4, CH_2). (Found C, 51·29; H, 6·91; S, 13·48. Calcd for $C_{10}H_{16}SO_4$: C, 51·77; H, 6·95; S, 13·82%.)

3,3,6,6-Tetramethyl-1-thiacycloheptane-4,5-dione-1-oxide (3) was obtained by a circuitous route. 3,3,6,6-Tetramethyl-5-hydroxy-1-thiacycloheptan-4-one[2] (3 g, 10 mmoles) was dissolved in 10 ml of a pyridine-water mixture (4:1). To this well-stirred soln was added dropwise dichloroiodobenzene (6 g, 21·8 mmole) dissolved in 10 ml pyridine. After several hr standing, chloroform was added, the soln was washed twice with dil H_2SO_4aq, once with water, and thereafter was dried over $MgSO_4$. Removal of the solvent left in near quantitative yield crude 3,3,6,6-tetramethyl-5-hydroxy-1-thiacyclohepta-4-one-1-oxide, NMR (C_6H_6) δ 1·01 (s, 6, CH_3), δ 1·07 (s, 3, CH_3), δ 2·53 (s, 2, CH_2), and δ 2·56 (s, 2, CH_2). The rest of the spectrum was not recorded. The material was quite unstable.

The crude hydroxysulfide (1 g, 3·0 mmole) was treated with $Pb(OAc)_4$ (1·6 g, 4 mmoles) in 10 ml pyridine. After 2 days standing the mixture was worked up by adding 50 ml water followed by dil HCl aq (cooling) until the soln was acidic. The resulting soln was extracted 5 times with chloroform, the organic layer was washed with $NaHCO_3$ aq followed by water. After drying over $MgSO_4$, the crude product was chromatographed over silica gel using chloroform as eluent. Analytically pure sulfoxide was obtained by dissolving this product in a minimal amount of CH_2Cl_2. An equal amount of n-heptane was added and the solvent was evaporated to half the original volume. More n-heptane was added until crystallization began whereupon the soln was cooled to −30°. In this manner there was obtained 195 mg (0·59 mmole, 20%) of 3, mp 123–124·5°, UV (EtOH) 329 nm (ε 17) and 304 nm (ε 21), NMR (CCl_4) δ 1·39 (s, 12, CH_3) and δ 3·02 (s, 4, CH_2). (Found C, 55·65; H, 7·46, S, 14·70. Calcd for $C_{10}H_{16}O_3S$: C, 55·61; H, 7·47; S, 15·5%.)

3,3,5,5-Tetramethyl-1-thiacyclohexa-4-one-1,1 dioxide (10) was prepared by oxidation of 7[3] by the procedure described for 4.

Irradiation of 1 was carried out usually with $5 \cdot 10^{-3}$ M soln in benzene using for preparative reactions a medium pressure lamp with a quartz cooling jacket. The course of reaction was followed gas chromatographically. Four new peaks developed during irradiation. The mixture was separated into its components by preparative gas chromatography (6′ SE-30, 15% on Chromosorb at 200°).

The chief product, 6, had IR (CCl_4) 2980, 2950, and 1740 cm^{-1}, NMR (CCl_4) δ 1·36 (s, 6, Me) and δ 2·73 (s, 2, CH_2), mass spectrum (70 ev) parent *m/e* 116 (calc for C_5H_8OS 116). The IR spectrum was superimposable on that of authentic 6.[9]

Compound 7 was identified by comparison of its spectra with those of authentic material.

The product 8 had IR (CCl_4) 2970, 2870, 2800, 2700, 1730, and 1645 cm^{-1}, NMR (CCl_4) δ 1·11 (s, 6, CH_3), δ 1·79 (m, 3, allylic CH_3), δ 2·47 (s, 2, CH_2), δ 3·04 (s, 2, CH_2), δ 4·82 (m, 2, vinyl H), and δ 9·35 (s, 1, $\overset{\overset{O}{\|}}{C}-\underline{H}$), mass spectrum *m/e* 172 (calcd for $C_9H_{16}OS$ 172). In the presence of Eu(DPM)$_3$ (*ca* 1 : 1) the Me groups adjacent to CO were shifted 4·43 ppm downfield, the allylic Me group was shifted 3·60 ppm downfield, one methylene group 0·57 ppm, the other 1·00 ppm, the vinylic protons were shifted downfield 2·58 and 0·11 ppm, respectively.

Aldehyde **9** had IR (CCl_4) 2970, 2870, 2800, 2700, 1730, and 1660 cm^{-1}, NMR (CCl_4) δ 1·12 (s, 6, Me), δ 1·73 (complex absorption, 6, allylic Me) δ 2·71 (s, 2, $C\underline{H}_2$), δ 5·52 (complex m, 1, vinyl H) and δ 9·35 (s, 1, $\overset{O}{\overset{\|}{C}}—\underline{H}$); mass spectrum (70 ev) *m/e* 172 (calcd for $C_9H_{16}OS$ 172). In the presence of Eu(DPM)$_3$ (*ca* 1 : 1) the Me peaks adjacent to CO were shifted 4·73 ppm downfield, the allylic Me groups gave separate absorptions at δ 1·24 and δ 1·78, the methylene group was shifted 0·1 ppm downfield, and the vinylic proton was shifted 1·88 ppm downfield.

Isobutene was determined by passing a N_2 stream through the soln during irradiation and leading the gas through a trap filled with Br_2 in CCl_4. After competition of the irradiation, the soln in the trap was worked up yielding 1,2-dibromo-2-methylpropane, identified by comparison with an authentic sample.

The presence of CO was demonstrated by sweeping the irradiated soln with N_2 and passing the gas stream through a soln of palladium chloride. The characteristic black complex quickly formed.

Irradiation of **7**, **4** *and* **10** were carried out under similar conditions and products were isolated by essentially the same GLPC procedures. The unsaturated aldehydes **11** and **12** were isolated in very small amounts of owing to difficulties in gas chromatographic separation. A mixture of **11** and **12** had IR (CCl_4) 3125, 3110, 2940, 2900, 2880, 2720, 1735, 1640, 1135, and 1120 cm^{-1}. Product **11** has NMR($CDCl_3$) δ 1·33 (s, 6, CH_3), δ 1·94 (broad s, 6, allylic $C\underline{H}_3$), δ 3·28 (s, 2, $C\underline{H}_2$), δ 5·30 (m, 1, vinylic H), and δ 9·08 (s, 1, $\overset{O}{\overset{\|}{C}}\underline{H}$). Saturation of the δ 1·94 absorption caused the vinylic absorption at δ 5·30 to collapse to a singlet; mass spectrum parent *m/e* 204 (calcd. for $C_9H_{16}O_3S$ 204). Product **12** has NMR ($CDCl_3$) δ 1·33 (s, 6, $C\underline{H}_3$), δ 2·17 (m, 3, allylic $C\underline{H}_3$), δ 3·15 (s, 2, $C\underline{H}_2$) δ 4·01 (s, 2, CH_2), δ 6·06 (m, 2, vinylic $\underline{H}$), and δ 9·08 (s, 1, $\overset{O}{\overset{\|}{C}}H$). Saturation of the Me resonance at 2·17 caused the vinylic absorption at δ 6·06 to collapse to a broad singlet; mass spectrum parent *m/e* 204 (calcd. for $C_9H_{16}O_3S$ 204).

Irradiation of **3** under a variety of experimental conditions failed to lead to any characterizable products. The reaction was not investigated further.

Irradiation of 3,3,7,7-tetramethylcycloheptane-1,2-*dione* (**2**) in benzene soln (not degassed) for about 18 hr followed by removal of the solvent resulted in about a 60% yield of 3,3,7,7-tetramethylcycloheptane-2-ol-1-one identified by comparison with authentic material.[7b] Moderate amounts of biphenyl were detected in the gas chromatogram as well as a trace amount of a component with the same retention time as 3,3,7,7-tetramethylcycloheptane-1,2-diol.

Quantitative determinations were done using a Rayonet photochemical reactor equipped with a turntable assembly. Experiments were carried out usually using lamps with emission maxima at 254 nm but for wavelength investigations 300 and 350 nm lamps were also used. Irradiations were carried out in quartz tubes which had been degassed by several freeze thaw cycles prior to irradiation.

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