Tetrahedron Vol. 37, No. 19, pp. 3269 to 3274, 1981
Printed in Great Britain.

0040-4020/81/193269-06$02.00/0
© 1981 Pergamon Press Ltd.

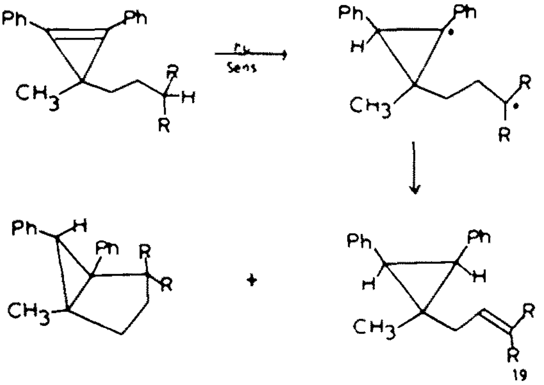
EFFECTS OF SUBSTITUENTS ON THE TYPE II PHOTOREACTION OF TETRASUBSTITUTED CYCLOPROPENES[1]

ALBERT PADWA* and CHUEN S. CHOU
Department of Chemistry, Emory University, Atlanta, GA 30322, U.S.A.

(*Received in USA April* 1981)

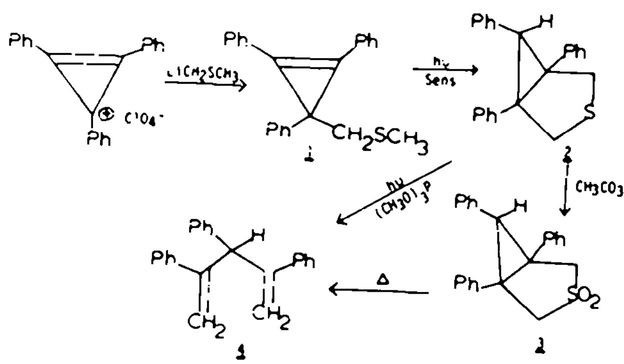
Abstract—The triplet sensitized behavior of a number of 3-alkyl substituted cyclopropenes containing a heteroatom on the side chain has been studied in mechanistic detail. The triplet state was found to undergo H-atom abstraction by a mechanism analogous to the well-known Norrish type II process of carbonyl compounds. Rate constants for H-abstraction were obtained by plotting Φ_0/Φ_q vs *trans*-stilbene at a constant quencher to cyclopropene ratio. The rate constants for H-abstraction were found to be two orders of magnitude less than that for related phenyl alkyl ketones and increased as the strength of the C–H bond in the γ-position decreased. The possibility of electron transfer from the heteroatom of the side chain to the π–π* triplet state is discussed.

Of known photochemical processes, H-abstraction has been surely one of the most intensively investigated reactions. Most studies have centered on the photochemistry of the CO group. These include the photoreduction[2] of ketones in solvents with abstractable hydrogens and the type II reaction of ketones possessing γ-hydrogens.[3] It is now generally accepted that the Norrish type II reaction proceeds by way of a n–π* triplet state.[4] Abstraction of the γ-H leads to a 1,4-biradical intermediate which may either (a) cyclize, (b) undergo cleavage to form an olefin and an enol, or (c) revert to the starting ketone by reabstraction of hydrogen.[5] Placement of a heteroatom adjacent to the γ C–H bond results in a pronounced acceleration of the rate of H-abstraction.[6–9] It is well known that heteroatoms interact with excited ketones in charge-transfer processes to form exciplexes in which the donor has radical cation character.[11,12] Thus, the first step in the photoelimination reaction of α-amino ketones and β-keto sulfides has been suggested to proceed by transfer of an electron from the heteroatom to the excited CO group.[7–9] In contrast to carbonyl compounds, examples of H-abstraction in the direct and sensitized photolysis of olefins are less common. Nevertheless, a number of reports have appeared in the literature which show that the excited π, π* state of certain olefins have the ability to abstract H.[13–15] In our previous studies dealing with cyclopropenes, we observed that the triplet sensitized irradiation of tetra-substituted cyclopropenes which possess γ-hydrogens lead to products involving intramolecular transfer of H from the side chain to the π–π* excited state.[16–18] The products obtained were explained as resulting from disproportionation and/or collapse of a biradical intermediate. The entropy of activation was typical of a reaction proceeding via a strain free 6-center transition state and the activation energy associated with the H-abstraction reaction was found to be dependent on the γ C–H bond strength.[19] In order to provide more detailed information concerning the nature of the H-abstraction, we have investigated the triplet sensitized irradiation of several cyclopropenes containing a heteroatom on the side chain with the hope of establishing the involvement of electron transfer with these systems. In this paper we describe some of the salient features associated with this reaction.

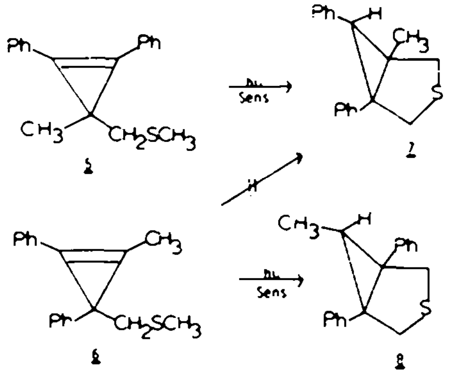


RESULTS AND DISCUSSION

3-Methylthiomethyl substituted cyclopropenes **1**, **5** and **6** were prepared by treating the appropriate cyclopropenyl cation with methylthiomethyllithium[19] according to the general procedure of Breslow *et al.*[20] The thioxanthone sensitized irradiation of cyclopropene **1** afforded 1,5,6-triphenyl-3-thiabicyclo-[3.1.0]hexane (**2**) in 90% yield as a crystalline solid, m.p. 203–204°. The identity of **2** was based on its characteristic NMR spectrum which showed a set of doublets at δ 3.30 (2H, J = 12.0 Hz) and 3.65 (2H, J = 12.0 Hz), a singlet at 3.47 (1H) and a multiplet at 6.69–7.45. Further support for this structure was obtained by the extrusion of the sulfur bridge to give 2,3,4-triphenyl-1,4-pentadiene (**4**). Thus the photolysis of **2** in trimethyl phosphite solvent, according to the procedure of Corey and Block,[21] afforded **4** in 80% yield. Diene **4** was also obtained from the thermolysis of 3-thiabicyclo[3.1.0]hexane-3,3-dioxide **3**. This material was readily prepared from **2** by oxidation with peracetic acid. The chelotropic extrusion of sulfur dioxide from the 3-thiabicyclo[3.1.0]hexane-3,3-dioxide system has been reported as a useful synthesis of 1,4-dienes.[22] We found that the flash vacuum pyrolysis of **3** at 625° gave diene **4** in 75% yield thereby providing additional support for the structure of the photoproduct.



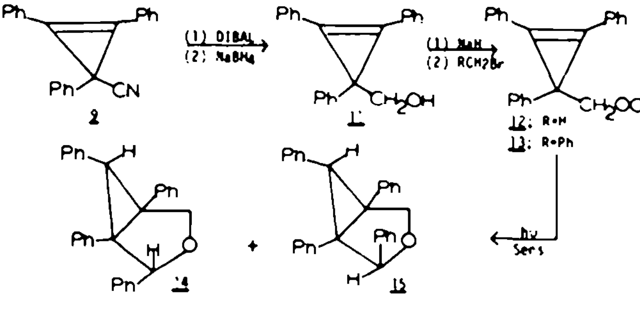
We also examined the triplet-induced photobehavior of cyclopropenes **5** and **6**. In each case the photoproduct obtained arises from intramolecular H atom transfer. The sensitized irradiation of cyclopropene **5** gave 1-methyl-5,6-diphenyl-3-thiabicyclo[3.1.0]hexane **7**. Photolysis of the unsymmetrically substituted cyclopropene **6** under similar conditions gave 1,5-diphenyl-6-methyl-3-thiabicyclo[3.1.0]hexane **8** as the exclusive photoproduct. No signs of the isomeric thiabicyclohexane **7** could be detected in the crude photolysate. The identity of thiabicyclohexane **8** was determined by its straightforward spectral characteristics [NMR (CDCl$_3$, 90 MHz) δ 1.08 (*d*, 3H, J = 7.0 Hz), 2.32 (*q*, 1H, J = 7.0 Hz), 3.25 (*d*, 2H, J = 12.0 Hz), 3.48 (*d*, 2H, J = 12.0 Hz) and 7.03–7.36 (*m*, 10H)].



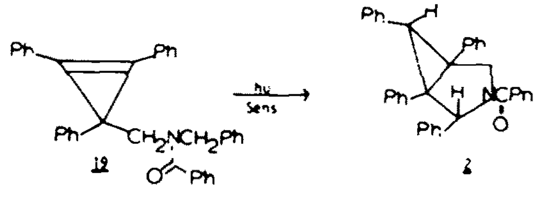
As our next goal, we decided to replace the S-atom present on the alkyl side chain with an O- and N-atom. This required a great deal of synthetic manipulation. Both N,N-dimethylaminomethyllithium[23] and methoxymethyllithium[24] were added to the cyclopropenyl perchlorates. Unfortunately, no characterizable products could be isolated. This problem was solved by synthesizing 1,2,3-triphenyl-3-cyanocyclopropene (**9**). This involved the addition of potassium cyanide to triphenylcyclopropenyl perchlorate in the presence of 18-Crown-6. DIBAL reduction of **9** gave the 3-formyl substituted cyclopropene **10** which, in turn, was reduced with sodium borohydride to the corresponding alcohol. Application of the Williamson ether synthesis using **11** gave both methoxymethyl (**12**) and benzyloxymethyl (**13**) cyclopropenes.

The triplet sensitized irradiation of **12** gave back recovered starting material even after extended irradiation. The reluctance of cyclopropene **12** to undergo H-atom transfer is probably due to the difficulty of transferring a primary H-atom to the π–π^* triplet state of the cyclopropene. The sensitized irradiation of cyclopropene **13**, on the other hand, gave rise to a mixture of *exo*-(**14**) (75%) and *endo*-1,2,5,6-tetraphenyl-3-oxabicyclo[3.1.0]hexane (**15**) (25%). The structures of both isomers were determined on the basis of their characteristic NMR spectra: *exo*-**14** (δ 3.05 (*s*, 1H), 4.39 (*d*, 1H, J = 10.0 Hz), 4.50 (*d*, 1H, J = 10.0 Hz), 5.38 (*s*, 1H)); *endo*-**15** (δ 3.00 (*s*, 1H), 4.49 (*d*, 1H, J = 9.5 Hz), 4.76 (*d*, 1H, J = 9.5 Hz), 5.42 (*s*, 1H)).

The triplet induced behavior of a 3-carbinyldialkylamino substituted cyclopropene was also investigated. Treatment of 3-formyl-1,2-3-triphenylcyclopropene **10** with benzylamine afforded the expected N-benzylimine **16**. Attempts to reduce the C–N double bond with LAH gave cyclopropylamine **17**. Earlier work by Breslow *et al.* showed that treatment of a cyclopropenyl ester with LAH resulted in reduction of the 3-membered ring.[25] The reaction was suggested to involve coordination of the π-bond with the aluminum hydride. Presumably a similar mechanism is involved with cyclopropene **16**. When lithium borohydride was used as the reducing agent, N-benzyl-(1,2,3-triphenylcyclopropen-2-yl)carbinylamine **18** could be obtained in good yield. Treatment of **18** with benzoyl chloride gave benzamide **19** which

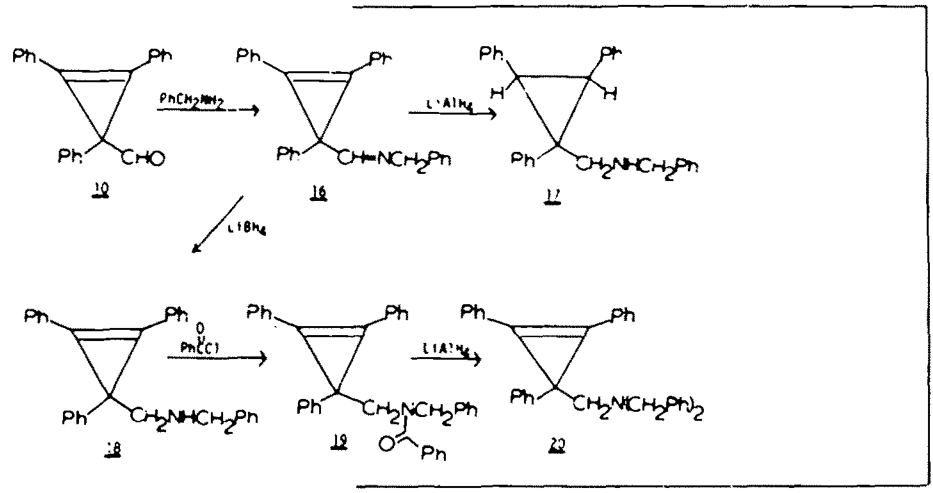


was smoothly reduced to N,N-dibenzylcarbinylamine **20** with LAH.



Irradiation of a sample of cyclopropene **20** with thioxanthone produced a complex mixture of products. All attempts to isolate a characterizable product from the crude photolysate failed. In contrast to the plethora of products obtained from **20**, the sensitized irradiation of benzamide **19** gave *exo* - 1,2,5,6 - tetraphenyl - 3 - benzoyl - 3 - azabicyclo[3.1.0]hexane (**2**) as the exclusive photo-product; NMR ($CDCl_3$, 90 MHz) δ 3.03 (*s*, 1H), 4.08 (*d*, 1H, J = 11.0 Hz), 4.58 (*d*, 1H, J = 11.0 Hz), 5.58 (*s*, 1H) and 6.20–7.66 (*m*, 25H).

The value of k_{CQ} in benzene is taken to be 5×10^9 $L mol^{-1}$.[28] Quantum yields and k_r values are given in Table 1 for the cyclopropenes studied. The data clearly show that the symmetrically 1,2-diphenyl substituted cyclopropenes all accept excitation from triplet thioxanthone with a reaction rate constant k_{SC} which is essentially diffusion controlled to give excited π–π^* states which have lifetimes, as measured by *trans*-stilbene quenching, of a few microseconds before transformation to product or to some biradical species (B) leading to product. If the biradical intermediate B, formed by hydrogen transfer, reverts to cyclopropene then the mechanism shown in Scheme 1 would have to be modified and the expression for Φ_0 would include a factor representing the fraction of biradicals that go on to product. This latter fraction is not known, though a minimum value for it is given by the reaction quantum yield. With the unsymmetrically substituted cyclopropene **6**, the quantum yield for abstraction was found to depend on the concentration of starting material, and consequently it was not possible to determine the rate of hydrogen transfer by Cristol's method.[27]



In order to derive additional mechanistic information concerning these intramolecular H-transfer reactions, a more quantitative investigation of these processes was undertaken. Quantum yields for product formation were determined using benzophenone–benzhydrol as the chemical actinometer.[26] Recently, Cristol *et al.* have described a method for the treatment of quenching data of photosensitized reactions which allows for the determination of the lifetime of the triplet state.[27] We have used this method to approximate the rate of H-transfer to the triplet state of the symmetrically 1,2-diphenyl substituted cyclopropene system. The kinetic expression for the triplet photosensitized reaction, involving sensitizer S_0, cyclopropene C_0 and quencher Q_0 to give bicyclo[3.1.0]hexane P, was derived from Scheme 1. The extent of conversion of triplet cyclopropene to product in benzene was studied as a function of the concentration of *trans*-stilbene as quencher. Plots of Φ_o/Φ_q at varying quencher concentration but with constant [Q]/[C] ratios ([Q]/[C] = 1/50) give lines whose intercepts afford k_{SQ}/k_{SC} ratios and whose slopes divided by the intercepts give k_{CQ^3} values. The modified Stern–Volmer plots obtained were linear with the slopes listed in Table 1 as $k_{CQ}\tau^3C$ values.

$$\Phi_o/\Phi_q = \left[1 + \frac{k_{SQ}[Q]}{k_{SC}[C]}\right] + \left[1 + \frac{k_{SQ}[Q]}{k_{SC}[C]}\right] k_{CQ}\tau^3C[Q].$$

The formation of the 3-heterobicyclo[3.1.0]hexane ring system from the triplet sensitized irradiation of the above cyclopropenes indicates that the sensitized reaction proceeds via a mechanism analogous to that ac-

$$S_0 \xrightarrow{h\nu} S^{*1} \xrightarrow{k_{isc}} S^{*3}$$

$$S^{*3} + C_0 \xrightarrow{k_{SC}} C^{*3} + S_0$$

$$S^{*3} + Q_0 \xrightarrow{k_{SQ}} Q^{*3} + S_0$$

$$S^{*3} \xrightarrow{k_{SD}} S_0$$

$$C^{*3} \xrightarrow{k_r} B \rightarrow P_0$$

$$C^{*3} \xrightarrow{k_d} C_0$$

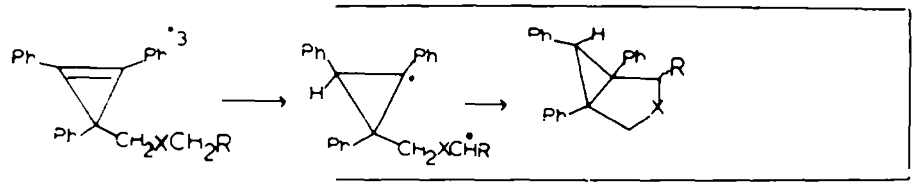
$$C^{*3} + Q_0 \xrightarrow{k_{CQ}} C_0 + Q^{*3}$$

Scheme 1.

Table 1.

Cyclopropene	$\phi^{c,d}$	$k_{CQ\tau}{}^{3c}, M^{-1e}$	$\tau, 10^{7} s^{-1}$	$k_r, 10^{6} s^{-1}$
1	0.042	2240	4.48	0.09
5	0.097	3660	7.32	0.13
6	0.17			
13	0.76	670	1.34	5.67
19	0.58	1040	2.08	2.79

(a) concentration of cyclopropene ca 1 × 10^{-2}M (b) 40°C (c) sum of all products (d) ± 10% (e) ± 20%



cepted for the Norrish type II reaction of ketones. Thus, the triplet state of cyclopropenes 1, 13 or 19 transfers a H from the γ-position of the side chain to produce a 1,5-biradical intermediate which subsequently collapses to give the observed photoproducts. Several results listed in Table 1 are of interest and merit comment. The relative rate constants for the triplet states of the cyclopropenes can be rationalized on the basis of structural considerations. Thus, the benzyloxymethyl substituted cyclopropene 13 transfers a hydrogen three times more readily than the closely related 3-phenylpropyl substituted system.[17] The larger rate constant associated with the H-transfer reaction of cyclopropene 13 is undoubtedly a reflection of the weaker bond dissociation energy of the γ C–H bond when it is adjacent to an O-atom. The failure to detect a reaction with the triplet state of cyclopropene 12 can also be readily understood since the activation energy associated with this reaction will be very large.[17] The high quatum efficiency associated with cyclopropenes 13 and 19 is fully compatible with the suggestion that the 1,5-biradical intermediate does not revert to starting material by reverse H-transfer. It is also of interest to note that the triplet lifetimes (see Table 1) of the cyclopropenes are several hundred times greater than those for the related phenyl alkyl ketones.[3,4] The longer lifetime of the cyclopropenes may very well reflect the weaker C–H bond being formed in the abstraction reaction. In addition, the rate of H-abstraction is significantly less than that for the phenyl ketone system. The much lower rate constant for H-abstraction is probably related to radical delocalization of the triplet state by the attached phenyl groups and perhaps to a lower reactivity of the planar π–π* state.

We had previously noted that transfer of a primary H-atom from the γ-position to the π–π* triplet state of the cyclopropene does not occur.[17] This was attributed to the large activation energy associated with this reaction. Our results with the methylthiomethyl cyclopropenes 1 and 5 show, however, that these systems do undergo H-atom transfer. One possibility to account for the higher reactivity of the 3-hetero substituted cyclopropene system is that the excited π,π* triplet state interacts with the electrons on the heteroatom to form a charge-transfer complex. Once formed, the charge transfer complex can transfer a proton from the γ-position to give the 1,5-biradical intermediate.

One final point worth mentioning is that the sensitized irradiation of the unsymmetrically substituted cyclopropene 6 proceeds via H-transfer to the carbon bearing the Me group. The complete regiospecificity of the reaction is undoubtedly related to the fact that the diradical produced on hydrogen transfer to the Me bearing C atom allows maximum delocalization of the radical centers in the resulting diradical intermediate.

In conclusion, the results obtained from this investigation indicate that triplet states of tetrasubstituted cyclopropenes possessing γ-hydrogens adjacent to heteroatoms undergo ready intramolecular H-transfer. The rate constants for the H-abstraction reaction were found to be quite high. We are continuing to examine the H-transfer reaction and will report additional findings at a later date.

EXPERIMENTAL[29]

Preparation and triplet sensitized irradiation of 1,2,3-triphenyl-3-methylthiomethylcyclopropene (1). To a soln containing 3.6 ml of a 1.4 M n-BuLi soln in hexane was added 0.58 g tetramethylenediamine. The soln was kept at 20° and then 5 ml dimethyl sulfide was added. The mixture was stirred for 4.5 hr and was then added to a suspension containing 750 mg triphenylcyclopropenyl perchlorate in 50 ml tetrahydrofuran. After stirring at 20° for 4 hr, the excess Li reagent was destroyed by the addition of MeOH. The organic layer was extracted with ether, washed with water and dried over $MgSO_4$. Removal of the solvent left 650 mg of 1 as a crystalline solid, m.p. 66–67°; IR (KBr) 3.28, 3.45, 5.52, 6.24, 6.75, 7.00, 8.15, 9.50, 9.90, 11.15 and 13.50 μ; UV (95% EtOH) 228, 314 and 330 nm (ε 26100, 24700 and 21500); NMR ($CDCl_3$, 60 MHz) δ 2.02 (*s*, 3H), 3.50 (*s*, 2H) and 6.98–7.85 (*m*, 15H); *m/e* 328 (M^+), 313, 267, 205, 204, 178 and 77 (base). (Found: C, 84.05; H, 6.14. Calc. for $C_{23}H_{20}S$: C, 84.10; H, 6.14%).

A soln containing 120 mg of the above cyclopropene and 15 mg thioxanthone in 170 ml benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium glass filter for 1 hr under an argon atmosphere. Removal of the solvent left a yellow oil which was subjected to silica gel chromatography using hexane as the eluent. The major component isolated contained 108 mg (90%) 2 as a crystalline solid, m.p. 203–204°; IR (KBr) 3.25, 6.27, 6.98, 7.28, 9.45, 9.80, 10.20, 10.63, 13.35, 14.04 and 14.81 μ; NMR ($CDCl_3$, 60 MHz) δ 3.30 (*d*, 2H, J = 12.0 Hz), 3.47 (*s*, 1H), 3.65 (*d*, 2H, J = 12.0 Hz) and 6.69–7.45 (*m*, 15H); *m/e* 328 (M^+), 205, 204 and 77. (Found: C, 84.16; H, 6.18. Calc. for $C_{23}H_{20}S$: C, 84.10; H, 6.14%).

Further support for the structure of 2 was obtained by a photoextrusion reaction of sulfur. A soln containing 100 mg of 2 and 10 ml trimethylphosphite was irradiated in a Quartz tube with a 450-W Hanovia lamp equipped with a Vycor filter sleeve for 33 hr. The excess trimethylphosphite was removed under reduced pressure and crude mixture was chromatographed on a silica gel column using a 5% ether–hexane mixture as the eluent. The major component isolated contained 80 mg of a colorless oil whose structure was assigned as 4; IR (neat) 3.28, 3.31, 6.20, 6.32, 6.40, 6.75, 6.95, 7.00, 7.20, 7.32, 9.56, 9.85, 11.25, 13.31, 13.80 and 14.70 μ; UV (95% EtOH) 240 nm (ε 18000); NMR ($CDCl_3$, 60 MHz) δ 4.98 (*s*, 2H), 5.21 (*s*, 1H), 5.63 (*s*, 2H) and 7.0–7.57 (*m*, 15H); *m/e* 296 (M^+), 219, 202, 115, 91 and 77. (Found: C, 93.10; H, 6.82. Calc. for $C_{23}H_{20}$: C, 93.20; H, 6.80%).

Compound 4 was also prepared from the pyrolysis of 3. A soln containing 148 mg of 2, 2 ml AcOH and 2 ml 10% H_2O_2 was heated at 90° for 2 hr. The mixture was cooled and then an additional 1 ml of 10% H_2O_2 was added. After heating for 2 hr the soln was diluted with 10 ml water and was extracted with ether. The ether layer was washed with water and dried over $MgSO_4$. Removal of the solvent under reduced pressure left 135 mg (65%) of a crystalline solid, m.p. 169–170°, whose structure was assigned as 3; IR (KBr) 3.28, 3.66, 6.30, 6.78, 7.00, 7.80, 8.18, 8.80, 11.30, 12.81, 13.45 and 14.82 μ; NMR ($CDCl_3$, 60 MHz) δ 3.17 (*s*, 1H), 3.57 (*d*, 2H, J = 14.0 Hz), 3.85 (*d*, 2H, J = 14.0 Hz) and 6.33–7.26 (*m*, 15H).

A 350 mg sample of 3 was heated in a flash vacuum pyrolysis apparatus at 0.003 nm with the oven held at 625°. The material that was collected on the liquid nitrogen cold finger was identical in every detail with a sample of 4 isolated from the photolysis of 2 in the presence of trimethylphosphite.

Preparation of 1,2 - *diphenyl* - 3 - *methyl* - 3 - *methylthiomethylcyclopropene* (5) *and* 1,3 - *diphenyl* - 2 - *methyl* - 3 - *methylthiomethylcyclopropene* (6). To a suspension containing 3.0 g methyldiphenylcyclopropenyl perchlorate in 200 ml tetrahydrofuran at −78° was added 0.02 Mole methylthiomethyllithium-TMEDA soln in tetrahydrofuran. The mixture was stirred at −78° for 4 hr and was then quenched by the addition of MeOH. The organic layer was taken up in ether, washed with water and dried over $MgSO_4$. Removal of the solvent under reduced pressure left a yellow oil which was subjected to silica gel chromatography using a 5% benzene–hexane mixture as the eluent. The first fraction isolated contained 840 mg (32%) of 5 as a clear oil; IR (neat) 3.26, 5.56, 6.30, 6.75, 6.96, 7.35, 8.12, 9.46, 11.08, 13.51, 13.92 and 14.91 μ; UV (95% EtOH) 228, 318 and 334 nm (ε 13200, 23200 and 14400); NMR ($CDCl_3$, 60 MHz) δ 1.57 (*s*, 3H), 2.05 (*s*, 3H), 2.98 (*s*, 2H) and 7.30–7.86 (*m*, 10H); *m/e* 251, 205 and 77. (Found: C, 81.08; H, 6.87. Calc. for $C_{18}H_{18}S$: C, 81.17; H, 6.81%).

The second component isolated from the column contained 1.66 g (64%) of a clear oil whose structure was assigned as 6; IR (neat) 3.25, 5.40, 6.26, 6.71, 6.94, 7.06, 8.08, 9.38, 11.10, 13.32 and 14.30 μ; UV (95% EtOH) 260 nm (ε 16000); NMR ($CDCl_3$, 60 MHz) δ 2.02 (*s*, 3H), 2.30 (*s*, 3H), 3.28 (*s*, 2H) and 7.0–7.65 (*m*, 10H); *m/e* 266, 251, 205 (base) and 77. (Found: C, 81.09; H, 6.85. Calc. for $C_{18}H_{18}S$: C, 81.17; H, 6.81%).

Triplet sensitized irradiation of 1,2 - *diphenyl* - 3 - *methyl* - 3 - *methylthiomethyl* - *cyclopropene* (5). A soln containing 125 mg of 5 and 15 mg thioxanthone in 200 ml benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium glass filter sleeve for 2 hr under an argon atmosphere. The solvent was concentrated under reduced pressure and the residue was chromatographed on a silica gel column using a 5% benzene–hexane mixture as the eluent to give 89 mg (75%) of 7 as a white crystalline solid, m.p. 124–125°; IR (KBr) 3.30, 3.42, 6.28, 6.75, 6.98, 7.30, 8.71, 9.45, 9.55, 9.82, 11.20, 13.31, 14.06 and 14.42 μ; UV (95% EtOH) 222 nm (ε 13000); NMR ($CDCl_3$, 90 MHz) δ 1.30 (*s*, 3H), 3.07 (*s*, 1H), 3.16 (*d*, 1H, J = 12.0 Hz), 3.30 (*s*, 2H), 3.36 (*d*, 1H, J = 12.0 Hz) and 6.63–7.46 (*m*, 10H); *m/e* 266, 251 and 77. (Found: C, 81/14; H, 6.83. Calc. for $C_{18}H_{18}S$: C, 81.17; H, 6.81%).

Triplet sensitized irradiation of 1,3*diphenyl* - 2 - *methyl* - 3 - *methylthiomethyl* - *cyclopropene* (6). A soln containing 110 mg of 6 and 15 mg thioxanthone in 170 ml benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium glass filter sleeve for 2 hr under an argon atmosphere. Removal of the solvent left a yellow oil which was subjected to silica gel chromatography using a 5% benzene–hexane mixture as the eluent. The major component isolated contained 67 mg (61%) of 8 as a clear oil: IR (neat) 3.26, 6.25, 6.70, 6.93, 9.40, 9.80, 13.82 and 14.61 μ; UV (95% EtOH) 280 nm (ε 2800); NMR ($CDCl_3$, 90 MHz) δ 1.08 (*d*, 3H, J = 7.0 Hz), 2.32 (*q*, 1H, J = 7.0 Hz), 3.25 (*d*, 2H, J = 12.0 Hz), 3.48 (*d*, 2H, J = 12.0 Hz) and 7.03–7.36 (*m*, 10H); *m/e* 266 (M^+), 251 (base), 189 and 77. (Found: C, 81.08; H, 6.85. Calc. for $C_{18}H_{18}S$: C, 81.17; H, 6.81%).

Preparation and triplet sensitized irradiation of 1,2,3 - *triphenyl* - 3 - *methoxy* - *methylcyclopropene* (12). To a soln containing 500 mg 9[10] in 40 ml benzene at 5° was added 1.35 ml of a 25% soln of DIBAL in toluene. The mixture was stirred at 25° for 2 hr and was then quenched with a NH_2Claq. The organic layer was taken up in ether, washed with water and dried over $MgSO_4$. Removal of the solvent left 340 mg (68%) of a labile oil which was assigned as 10: IR (neat) 3.25, 3.40, 5.89, 6.18, 6.28, 6.70, 6.95, 9.30, 9.45, 9.80, 11.20, 13.50 and 14.81 μ; NMR ($CDCl_3$, 90 MHz) δ 9.42 (*s*, 1H) and 6.83–7.80 (*m*, 15H). The above aldehyde was reduced at 0° with $NaBH_4$. Standard workup gave 11 in 85% yield as a clear oil; IR (neat) 2.92, 3.26, 3.40, 5.50, 6.28, 6.72, 6.92, 9.42, 9.80, 11.21, 13.50 and 14.81 μ; UV (95% EtOH) 332, 315 and 228 nm (ε 21000, 24700 and 26000); NMR ($CDCl_3$, 90 MHz) δ 1.53 (*br. s*, 1H), 4.47 (*s*, 2H) and 7.06–7.90 (*m*, 15H): *m/e* 298 (M^+), 267 (base) and 77. (Found: C, 88.42; H, 6.23. Calc. for $C_{22}H_{18}O$: C, 88.56; H, 6.08%).

To a soln containing 103 mg of the above alcohol in 15 ml tetrahydrofuran was added 40 mg NaH. To this soln was added 1 ml hexamethylphosphoramide and 3 ml MeI. The soln was stirred at 45° for 5 hr and was then subjected to an aqueous workup. The crude oil obtained was chromatographed on a silica gel column using a 5% acetone–hexane mixture as the eluent to give 82 mg (76%) of 12 as a clear oil; IR (neat) 3.25, 5.49, 6.28, 6.71, 6.92, 8.42, 9.20, 9.80, 10.41, 13.43 and 14.86 μ; UV (95% EtOH) 330, 314 and 228 nm (ε 19000, 23300 and 23200); NMR ($CDCl_3$, 60 MHz) δ 3.39 (s, 3H), 4.11 (*s*, 2H) and 6.97–7.86 (*m*, 15H); *m/e* 312 (M^+), 297 and 267. (Found: C, 88.10; H, 6.78. Calc. for $C_{23}H_{20}O$: C, 88.42; H, 6.45%).

The triplet sensitized irradiation of 12 with thioxanthone for 16 hr gave back recovered starting material.

Perparation and triplet sensitized irradiation of 1,2,3 - *triphenyl* - 3 - *benzyloxymethylcyclopropene* (13). Treatment of 12 with NaH followed by reaction of the alkoxide with benzyl bromide according to the procedure used above gave a 65% of 13 as a white crystalline solid, m.p. 92–93°; IR (KBr) 3.25, 5.50, 6.28, 6.78, 6.92, 7.40, 8.43, 9.25, 9.46, 9.88, 11.21, 13.48 and 14.81 μ; UV (95% EtOH) 331, 314 and 228 nm (ε 22800, 27000 and 25300); NMR ($CDCl_3$, 90 MHz) δ 4.20 (*s*, 2H), 4.60 (*s*, 2H) and 7.08–7.75 (*m*, 20H); *m/e* 388 (M^+, base) and 267. (Found: C, 89.50; H, 6.31. Calc. for $C_{29}H_{24}O$: C, 89.65; H, 6.23%).

A soln containing 72 mg of 13 and 10 mg thioxanthone in 170 ml benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium glass filter sleeve for 1.5 hr. Removal of the solvent followed by silica gel chromatography using a 5% ether–hexane mixture as the eluent gave two compounds. The first material eluted contained 53 mg (73%) of a clear oil whose structure was assigned as *exo*-14; IR (neat) 3.25, 6.25, 6.70, 6.92, 9.35, 9.45, 9.80, 13.41 and 13.84 μ; NMR ($CDCl_3$, 90 MHz) δ 3.05 (*s*, 1H), 4.39 (*d*, 1H, J = 10.0 Hz), 4.50 (*d*, 1H, J = 10.0 Hz), 5.38 (*s*, 1H) and 6.33–7.45 (*m*, 20H); *m/e* 388$^+$), 387, 311 and 77. (Found: C, 89.93; H, 6.25. Calc. for $C_{29}H_{24}O$: C, 89.65; H, 6.23%).

The second fraction isolated from the column contained 18 mg (26%) of *endo*-15 as a colorless oil; IR (neat) 3.21, 6.25, 6.70, 6.91, 9.50, 9.65, 13.32 and 13.67 μ; NMR ($CDCl_3$, 90 MHz) δ 3.00 (*s*, 1H), 4.49 (*d*, 1H, J = 9.0 Hz), 4.76 (*d*, 1H, J = 9.0 Hz), 5.42 (*s*, 1H) and 6.30–7.46 (*m*, 20H); *m/e* 388 (M^+), 311 and 77 (base). (Found: C, 89.37; H, 6.52. Calc. for $C_{29}H_{24}O$: C, 89.65; H, 6.23%).

Preparation and triplet sensitized irradiation of N,N - *dibenzyl*

- (1,2,3 - *triphenyl - cyclopropen - 2 - yl)carbinylamine* (20). A soln containing 340 mg of 10, 3 ml benzylamine, 2.0 g K_2CO_3 carbonate and 3 drops glacial AcOH in 100 ml ether was stirred at 25° for 10 hr. Standard aqueous workup left a yellow solid which was recrystallized from MeOH to give 265 mg (60%) of the N-benzylimine of 16, m.p. 127–128°; IR (KBr) 3.24, 5.44, 6.08, 6.25, 6.70, 6.90, 7.28, 7.68, 8.68, 8.92, 9.45, 9.99, 11.05, 13.02, 13.24 and 14.51 μ; UV (95% EtOH) 329, 313, 266 nm (ϵ 21100, 23200 and 18700); NMR ($CDCl_3$, 90 MHz) δ 4.70 (*s*, 2H) and 7.2–8.1 (*m*, 16H); *m/e* 385 (M^+), 308, 294 and 267 (base). (Found: C, 90.18; H, 6.06; N, 6.61. Calc. for $C_{29}H_{23}N$: C, 90.35; H, 6.01; N, 7.00%).

Attempts to reduce the C–N double bond of 16 with LAH resulted in reduction of the cyclopropene ring to give 17, m.p. 119–120°; IR (KBr) 3.24, 6.25, 6.70, 6.90, 8.58, 8.70, 9.35, 9.80, 11.05, 13.32 and 14.59 μ; UV (95% EtOH) 268 nm (ϵ 11100); NMR ($CDCl_3$, 90 MHz) δ 1.60 (*br. s*, 1H), 2.75 (*s*, 2H), 2.95 (*s*, 2H), 3.86 (*s*, 2H) and 6.81–7.42 (*m*, 20H); *m/e* 389 (M^+), 299, 283 (base) and 269. (Found: C, 89.31; H, 7.04; N, 3.55. Calc. for $C_{29}H_{27}N$: C, 89.42; H, 6.99; N, 3.60%).

The over-reduction of the cyclopropene ring was circumvented by using lithium borohydride as the reducing agent. The reaction was carried out in ether to give 18 in 72% as a clear oil; IR (neat) 3.23, 5.22, 6.23, 6.75, 6.92, 7.40, 9.08, 9.45, 9.86, 11.10, 13.62 and 14.70 μ; UV (95% EtOH) 331, 313 and 226 nm (ϵ 19700, 23000 and 24600); NMR ($CDCl_3$, 90 MHz) δ 1.57 (*br. s*, 1H), 3.48 (*s*, 2H), 3.78 (*s*, 2H) and 7.87–6.86 (*m*, 20H).

To a soln containing 100 mg of the above amine, 20 ml Et_3N and 2.0 g K_2CO_3 in 30 ml ether was added 3 ml benzoyl chloride. Standard aqueous workup followed by silica gel column chromatography using a 8% acetone–hexane mixture as the eluent gave 19 in 54% yield as a crystalline solid, m.p. 136–137°; IR (KBr) 3.26, 5.52, 6.15, 6.28, 6.71, 6.92, 7.08, 7.70, 7.92, 8.53, 8.78, 9.80, 11.15, 13.40, 13.92 and 14.78 μ; UV (95% EtOH) 331, 313, 273 and 228 nm (ϵ 14700, 19300, 34000 and 26300); NMR ($CDCl_3$, 90 MHz) δ 4.20 (*br. s*, 2H), 4.53 (*br. s*, 2H) and 6.76–8.27 (*m*, 25H); *m/e* 492 (M^+), 401, 387, 280, 267 and 105. (Found: C, 87.72; H, 6.00; N, 2.80. Calc. for $C_{36}H_{29}NO$: C, 87.95; H, 5.94; N, 2.85%).

To a soln containing 100 mg of the above N-benzoylamine in 30 ml ether was added 30 mg LAH. After stirring for 10 hr at 25°, the reaction was quenched with water. The organic layer was taken up in ether and dried over $MgSO_4$. Removal of the solvent under reduced pressure left a yellow solid which was recrystallized from hexane to give 20 as a crystalline solid, m.p. 149–150°; IR (KBr) 3.26, 5.50, 6.27, 6.71, 6.90, 7.25, 7.40, 7.50, 7.68, 8.45, 9.10, 9.40, 9.80, 10.31, 11.20, 13.43 and 14.61 μ; UV (95% EtOH) 331 nm (ϵ 19900, 24300 and 30000); NMR ($CDCl_3$, 90 MHz) δ 3.40 (*s*, 2H), 3.50 (*s*, 4H) and 7.03–7.70 (*m*, 25H); *m/e* 478 (M^+), 477 (base) and 267. (Found: C, 90.45; H, 6.62; N, 2.89. Calc. for $C_{36}H_{31}N$: C, 90.52; H, 6.54; N, 2.93%).

All attempts to isolate a characterizable product from the sensitized irradiation of 20 failed.

Triplet sensitized irradiation of N - *benzyl* - N - *benzoyl* - (1,2,3 *triphenylcyclopropen - 2 - yl)carbinylamine* (19). A soln containing 178 mg of 19 and 20 mg thioxanthone in 100 ml benzene was irradiated with a 200-W Hanovia lamp equipped with a Uranium glass filter sleeve for 30 min. Removal of the solvent under reduced pressure left a yellow oil which was subjected to preparative thick layer chromatography using a 8% acetone–hexane mixture as the eluent. The major fraction isolated from the plate contained 137 mg of *exo*-21 as a crystalline solid, m.p. 144–145°, IR (KBr) 3.26, 6.10, 6.28, 6.73, 6.94, 7.28, 7.45, 8.55, 9.30, 9.80, 13.60 and 14.60 μ; NMR ($CDCl_3$, 90 MHz) δ 3.03 (*s*, 1H), 4.08 (*d*, 1H, J = 11.0 Hz), 4.58 (*d*, 1H, J = 11.0 Hz), 5.58 (*s*, 1H) and 6.20–7.66 (*m*, 25H); *m/e* 492 (M^+), 491 (base), 400, 386, 370, 358, 282 and 268. (Found: C, 87.77; H, 6.00; N, 2.82. Calc. for $C_{36}H_{29}NO$: C, 87.95; H, 5.94; N, 2.85%).

Quantum yield determinations. Quantum yields were determined using a "merry-go-round" apparatus[31] equipped with a 450-W Hanovia lamp housed in a quartz well at the center of the carriage. Samples in 13-nm Pyrex test tubes were degassed to 5×10^{-3} mm in five freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum yield determinations. An actinometer yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 M.[32] For the sensitized runs a filter soln of potassium dichromate in K_2CO_3aq was circulated through the well and the entire unit allowed to run for 1 hr prior to use.[32] A Uranium glass filter sleeve and Corning 7-54 filters were also used in conjunction with the filter soln. The concentrations were adjusted so that the sensitizer absorbed more than 98% of the light. Analyses were performed by quantitative NMR spectroscopy. The conversions were run to 25% or less. The mass balance in these runs was generally better than 98%. *trans*-Stilbene was used as the triplet quencher in the Stern–Volmer plots.

REFERENCES

[1] Photochemical Transformations of Small Ring Compounds. 119. For part 118, see A. Padwa, T. J. Blacklock, D. M. Cordova and R. Loza, *J. Am. Chem. Soc.* 1981.

[2] N. J. Turro, *Modern Molecular Photochemistry*, p. 362. Benjamin-Cummings, Menlo Park, California (1978).

[3] P. J. Wagner, *Accounts Chem. Res.* 4, 168 (1971).

[4] J. C. Scaiano, E. A. Lissi and M. V. Encina, *Rev. Chem. Intermediates* 2, 139 (1978).

[5] P. J. Wagner, *Rearrangements in Ground and Excited States* (Edited by P. deMayo), Vol. 3, p. 402. Academic Press, New York (1980).

[6] F. D. Lewis and N. J. Turro, *J. Am. Chem. Soc.* 92, 311 (1970).

[7] P. J. Wagner, A. E. Kemppainen and T. Jellinek, *Ibid.* 94, 7512 (1972).

[8] A. Padwa, W. Eisenhardt, R. Gruber and D. Pashayan, *Ibid.* 91, 1857 (1969).

[9] A. Padwa and D. Pashayan, *J. Org. Chem.* 36, 3550 (1971).

[10] S. G. Cohen, A. Parola and G. H. Parsons, *Chem. Rev.* 73, 141 (1973).

[11] S. G. Cohen and R. J. Baumgarten, *J. Am. Chem. Soc.* 89, 3741 (1967); S. G. Cohen and H. M. Chao, *Ibid.* 90, 165 (1968); S. G. Cohen, N. Stein and H. M. Chao, *Ibid.* 90, 521 (1969); S. G. Cohen and G. Parsons, *Ibid.* 92, 7603 (1970).

[12] R. S. Davidson and P. F. Lambeth, *Chem. Commun.* 1265 (1967); 511 (1968).

[13] H. M. Rosenberg and P. Serve, *J. Am. Chem. Soc.* 92, 4746 (1970).

[14] H. Morrison and F. Scully, *Chem. Commun.* 529 (1973).

[15] J. M. Hornback, *J. Am. Chem. Soc.* 96, 6773 (1974); *Tetrahedron Letters* 3389 (1976); J. M. Hornback, L. G. Mawhorter, S. E. Carlson and R. A. Bedont, *J. Org. Chem.* 44, 3698 (1979).

[16] A. Padwa, U. Chiacchio and N. Hatanaka, *J. Am. Chem. Soc.* 100, 3928 (1978).

[17] A. Padwa, T. J. Blacklock, C. S. Chou and N. Hatanaka, *Ibid.* 100, 5743 (1979).

[18] A. Padwa and C. S. Chou, *Ibid.* 102, 3619 (1980).

[19] D. J. Peterson, *J. Org. Chem.* 32, 1717 (1967).

[20] R. Breslow, H. Hover and H. W. Chang, *J. Am. Chem. Soc.* 84, 3168 (1962).

[21] E. J. Corey and E. Block, *J. Org. Chem.* 34, 1233 (1969).

[22] W. L. Mock, *J. Am. Chem. Soc.* 92, 6918 (1970).

[23] D. J. Peterson, *J. Organometal. Chem.* 21, 63 (1970).

[24] U. Schollkopf and H. Kuppers, *Tetrahedron Letters* 1503 (1964).

[25] R. Breslow, J. Lockhart and A. Small, *J. Am. Chem. Soc.* 84, 2793 (1962).

[26] W. M. Moore and M. Ketchum, *Ibid.* 84, 1368 (1962).

[27] S. J. Cristol and R. P. Micheli, *Ibid.* 100, 850 (1978).

[28] P. J. Wagner, P. A. Kelson, A. E. Kemppainen and R. G. Zepp, *Ibid.* 94, 7500 (1972).

[29] All m.ps are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga. The IR absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The UV spectra were measured with a Cary 14 Model 14 recording spectrophotometer using 1-cm matched cells. The PMR spectra were determined at 90 MHz using a Varian EM-390 spectrometer. All irradiations were carried out using a 450-W Hanovia medium-pressure mercury arc lamp.

[30] R. Breslow and C. Yuan, *J. Am. Chem. Soc.* 80, 5991 (1958).

[31] F. G. Moses, R. S. H. Liu and B. M. Monroe, *Mol. Photochem.* 1, 245 (1969).

[32] P. J. Wagner and T. J. Nakahira, *J. Am. Chem. Soc.* 96, 3668 (1974).