

79664-26-9; **3a**, 79072-70-1; **3a** permethyl derivative, 79664-27-0; **3b**, 79664-28-1; **3b** permethyl derivative, 79664-29-2; **3c**, 79664-30-5; **3c** permethyl derivative, 79664-31-6; **3d**, 79664-32-7; **3d** permethyl derivative, 79664-33-8; **3e**, 79664-34-9; **3e** permethyl derivative, 79664-35-0; **4a**, 79664-36-1; **4a** permethyl derivative, 79664-37-2; acetone, 67-64-1; decanal, 112-31-2; benzaldehyde, 100-52-7; cyclohexanone, 108-94-1; octanal, 124-13-0; 2,3-dimethoxybenzoyl chloride, 7169-06-4.

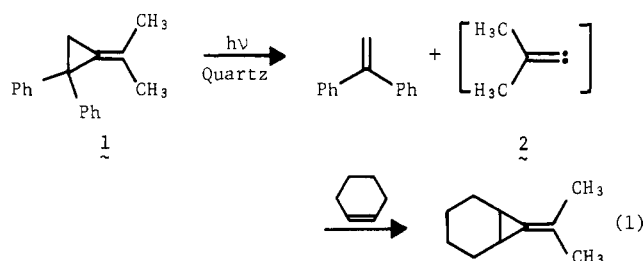
Photochemical Fragmentation of a Methylenecyclopropane¹

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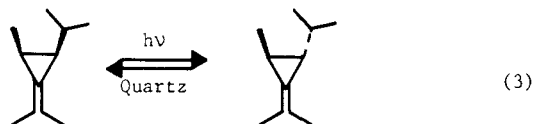
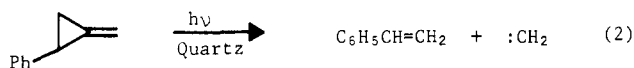
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Several years ago we reported that 2,2-diphenyl-1-isopropylidenecyclopropane (**1**) undergoes photofragmentation to give 1,1-diphenylethene and, presumably, 2-methylpropenylidene (**2**), which could be trapped by alkenes (eq 1).³ Owing to polymerization of the 1,1-di-



phenylethene during the course of the photolysis, it was not possible to assess the efficiency of trapping of **2**. Moreover, it was unclear from the previous study³ whether it was electronic excitation of the aryl or the ethylenic chromophore (or both) that was responsible for the fragmentation.

Ample precedent exists for the proposition that excitation of the former chromophore leads to fragmentation of three-membered rings.⁴ As an example, irradiation of phenylcyclopropane affords styrene and methylene (eq 2).⁵



The possibility that excitation of the ethylenic chromophore could lead to ring cleavage was suggested by the observation that photolysis of *cis*-3-methyl-2-isopropyl-1-isopropylidenecyclopropane caused its conversion to the *trans* isomer (eq 3).⁶ We wished, therefore, to examine

(1) Partial support of this research by the Robert A. Welch Foundation is gratefully acknowledged.

(2) Taken in part from the M.A. thesis of T.L., submitted in partial fulfillment of the degree requirements.

(3) Gilbert, J. C.; Butler, J. R. *J. Am. Chem. Soc.* 1970, 92, 7493.

(4) Review: Griffin, G. W.; Bertoniere, N. R. *Carbenes* 1973, 1, 305-349.

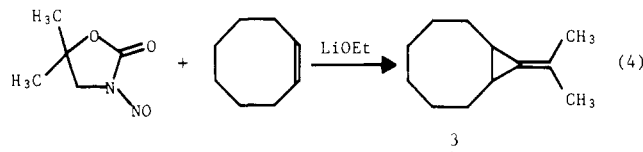
(5) (a) Richardson, D. B.; Durrett, L. R.; Martin, J. M., Jr.; Putnam, W. E.; Slaymaker, S. C.; Dvoretzky, I. *J. Am. Chem. Soc.* 1965, 87, 2763.

(b) ter Borg, A. P.; Razenberg, E.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* 1966, 85, 774.

the potential of photofragmentation in a substrate that lacked any aryl substituents. The results of that investigation are the subject of this paper.

Results and Discussion

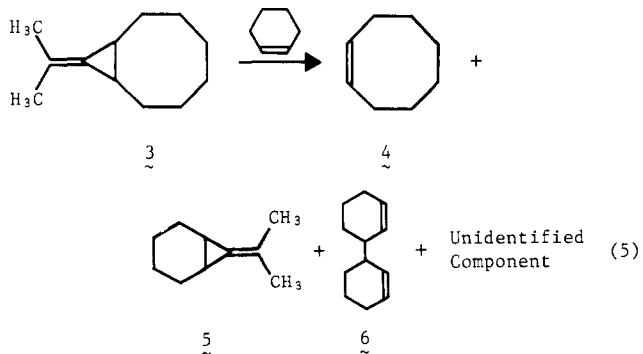
9-Isopropylidenebicyclo[6.1.0]nonane (**3**), the substrate selected for study of the potential of photofragmentation, was synthesized by use of the procedure previously reported by Newman (eq 4).⁷ The ultraviolet spectrum of



this methylenecyclopropane, as expected, does not have a maximum above 200 nm, but there is significant tailing to longer wavelengths with modest extinction coefficients: ϵ (hexane) 204 (220 nm), 165 (230 nm), 60 (240 nm), 30 (250 nm). Consequently, use of a 450-W medium-pressure Hanovia lamp is sufficient to achieve excitation of the ethylenic chromophore of **3**.

A preliminary experiment was executed to test for the photofragmentation of **3** and for the chemical efficiency of the process, assuming it occurred. To accomplish this, we irradiated a 0.15 vol % solution of **3** in cyclohexane through quartz with the aforementioned light source. After 12 h, 64% of **3** had been consumed, but cyclooctene, an expected fragmentation product, had been formed in only 17% yield. The approximately 30% yield of fragmentation product, based on consumption of starting material, remained constant for an additional 12 h of irradiation (see Experimental Section). Consequently, these observations suggest that photofragmentation of **3** occurs but is of only modest chemical efficiency.

To provide further support for the existence of photofragmentation, a 0.12 vol % solution of **3** in cyclohexane was photolyzed as before for a period of 26 h. Although no internal standard was present in this case, it appeared that disappearance of **3** was slower than before, presumably owing to absorption of some of the light by the cyclohexene. Analysis of the reaction mixture by gas-liquid chromatography revealed, in addition to cyclohexene, the presence of **3** and four other major volatile components in the ratio 67:7:3:21:2, respectively. Although the last of these components could not be identified, the other three were assigned, respectively, as cyclooctene (**4**), 7-isopropylidenebicyclo[4.1.0]heptane (**5**), and bi-2-cyclohexen-1-yl (**6**, eq 5).



identified compound appears to be unrelated to photofragmentation of **3** as a control experiment showed that

(6) Butler, J. R., unpublished results cited in ref 3, footnote 14.

(7) Newman, M. S.; Patrick, T. B. *J. Am. Chem. Soc.* 1969, 91, 6461.

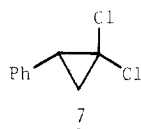
Table I. Ratio of 5 to 4 as a Function of Time of Photolysis

time, h	ratio ^a	time, h	ratio ^a
14	0.37	22	0.38
16	0.25	24	0.45
18	0.44	26	0.36

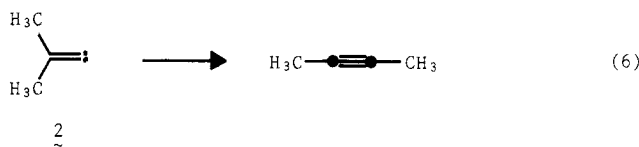
^a Peak areas were determined by the "cut and weigh" method. The raw data were corrected by multiplying the area for 4 by a calibration factor of 1.05.

they could also be produced by subjecting cyclohexene itself to the photolysis. The alkene 6 is believed to arise from an oxygen-initiated free-radical mechanism, as proposed by others;⁸ the oxygen presumably enters the argon-purged solution by diffusion through the Tygon tubing used in the apparatus. That cyclooctene was unreactive under the conditions of the photolysis was demonstrated by irradiation of a 0.10 vol % solution of it in cyclohexene, the result of which was production only of the two by-products known to arise from cyclohexene.

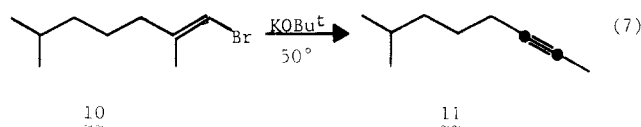
The ratio of 4 to 5 was monitored as a function of time by analysis of 2-mL aliquots removed periodically from the photolysis mixture. The results of these analyses are recorded in Table I. There is considerable scatter in these data, owing to the slow rate at which 3 undergoes photofragmentation, so that low absolute quantities of 4 and 5 are being analyzed. Nevertheless, the efficiency of transfer of the 2-methylpropenyldiene unit from 3 to cyclohexene is 35–40%, a value that compares quite favorably with that involving transfer of dichlorocarbene from 7 to cyclohexene, for which an efficiency of about 15% appears to obtain.⁹



An attractive rationale for production of 5 from the photolysis of 3 in cyclohexene involves extrusion of 2-methylpropenyldiene (2). If this is occurring, it might be expected that 2-butyne would be produced by rearrangement of the carbene (eq 6). The basis for this expectation



is the report that base-promoted α elimination at 50 °C of the vinyl bromide 8 affords, among other products, the alkyne 9 in 34% yield (eq 7),¹⁰ although the net 1,2 alkyl



shift that results from this α elimination may be a consequence of production of a carbenoid rather than of an unencumbered ("free") carbene. Perusal of the literature on unsaturated carbenes,¹¹ however, suggests that both

carbenoids and carbenes behave analogously with regard to rearrangements.

Repetition of the photolysis of 3 as a 0.09 vol % solution in cyclohexane with provision for trapping of effluent gases did, in fact, allow identification of 2-butyne as a product of the reaction, although quantitation of its yield was not possible. This result lends strong support to the contention that the carbene 2 is being produced. The approximate constancy of the ratio of 5 to 4 is also consistent with photofragmentation of 3 to give cyclooctene (4) and 2-methylpropenyldiene (2), which then partitions between rearrangement (eq 6) and cycloaddition to cyclohexene to afford 5.

It is concluded, therefore, that π - π^* excitation of a simple methylenecyclopropane, 3, by direct irradiation can lead to fragmentation to an alkene and an alkylidene-carbene, the latter being trappable by cycloaddition with an alkene. The electronic state of the carbene thus generated is presumably singlet, since others¹² have shown that attempts to initiate reactions of methylenecyclopropanes with triplet sensitizers fails to elicit either fragmentation³ or rearrangement.^{12,13} The inability to achieve photosensitized fragmentation, of course, does not constitute unambiguous evidence against extrusion of the triplet species as a result of direct photoexcitation of 3.

Experimental Section

A Varian Aerograph 90-P gas-liquid partition chromatograph equipped with a thermal-conductivity detector and with 0.25-in. columns was employed for analytical purposes. Helium was used as the carrier gas at a flow rate of 60 mL/min unless otherwise noted. The columns used contained 60/80 Chromosorb P (acid washed) as a solid support and were as follows: 1, 4 m, 30% TCEP; 2, 6 m, 30% SE-30; 3, 4 m, 15% FFAP; 4, 4 m, 15% β,β' -oxybis(propionitrile) on 60/80 firebrick.

Mass spectra were obtained on a Finnegan Model 4023 mass spectrometer operating at 70 eV.

The ultraviolet spectrum of 3 (quoted in Results and Discussion) was taken on a Cary 14 spectrophotometer.

Photochemical Apparatus. All photolyses were executed in a Pyrex apparatus equipped with a quartz immersion well surrounded by a cooling jacket. The light source was a Hanovia 450-W medium-pressure lamp. Purging of solutions with argon was performed prior to as well as throughout the period of irradiation.

Photolyses of 9-Isopropylidenebicyclo[6.1.0]nonane (3).
(A) In Cyclohexane. A solution of 330 mL of 3⁷ and 220 mL of cyclohexane was cooled to 10 °C and irradiated for 26 h; a 1-mL aliquot was removed every 2 h after the eighth hour, and 50 mL of a 0.14 M solution of adamantane in cyclohexane was added as a standard. Analysis of the resulting solutions by GLC [column 1 (90 °C)] revealed the presence of cyclooctene, cyclohexanol, and bicyclohexyl, each of which was identified by comparison of its retention volume and IR spectrum with those of an authentic specimen. The variation in product ratios and of recovered 3 as a function of time is shown in Table II. GLC peak areas from which these data are derived were determined by the "cut and weigh" method.

A solution of 450 μ L of 3 and 5 mL of cyclohexane was irradiated for 25 h at ambient temperatures. Exit gases were passed through a trap containing carbon tetrachloride held at 0 °C. Analysis by GLC [columns 2 (65 °C), 3 (70 °C), and 4 (70 °C)] showed that 2-butyne had been formed by comparison of its retention volume on each of the indicated columns with that of an authentic sample. GC/MS analysis of the solution also demonstrated the production of the alkyne.

(B) In Cyclohexene. A solution of 300 μ L of 3 and 250 mL of freshly distilled cyclohexene was cooled to 10 °C and irradiated for 26 h. Analysis of the photolysate by GLC [columns 1 (90 °C),

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Table II. Percentage of 3 and 4 as a Function of Time of Photolysis^a

time, h	%3	%4	fragmentation ratio ^b
0	100.0	0.0	
12	36.3	18.1	0.28
14	31.9	19.4	0.28
16	32.6	21.2	0.31
18	27.8	20.3	0.25
20	25.7	22.6	0.30
22	22.4	23.8	0.31
24	21.3	24.1	0.30

^a Adamantane was used as the standard; the area of peak for 4 was corrected by a calibration factor of 1.05.

^b Percent 4 formed/percent 3 consumed.

2 (190 °C), and 3 (89 °C)] showed the presence of 4, 5,⁷ and 6¹⁴ which were characterized by their identity with authentic specimens with regard to ¹H NMR and IR spectra and retention volumes on each of the three GLC columns indicated.

The photolysis was repeated, and 2-mL aliquots were removed after appropriate periods of time; analysis of them by GLC [column 1 (90 °C)] gave the data of Table I.

Photolysis of Cyclohexene. Irradiation at 10 °C of neat cyclohexene (5 mL), contained in a quartz ampule, for 25 h followed by GLC analysis [column 1 (139 °C)] showed formation of 6 and the same unidentified component as was produced by photolysis of 3.

Registry No. 3, 56666-90-1; 4, 931-88-4; 5, 53282-47-6; 6, 1541-20-4.

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Convenient Synthesis of Aryl Halides from Arylamines via Treatment of 1-Aryl-3,3-dialkyltriazenes with Trimethylsilyl Halides

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In recent years, the preparation of haloarenes from anilines or other arenes has departed radically from the early approach of Sandmeyer,² and halogenation methods involving metalation,³ in situ diazotization,⁴ halogen abstraction,⁴⁻⁸ and substitutive deamination⁹ have all been

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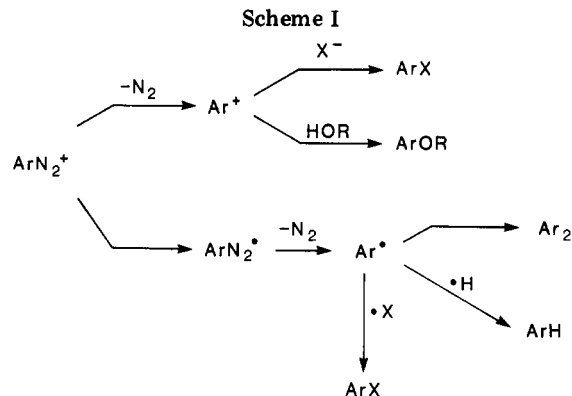
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^a All compounds were fully characterized by standard spectral methods. ^b Chemical yields reported are for isolated, chromatographically pure substances. Radiochemical yields of aromatic radioiodides (Ar¹²⁵I and/or Ar¹³¹I) are indicated in parentheses and refer to the conversion free radioiodide → aromatic radioiodide. Radiochemical purities were >99%. ^c Yields measured by HPLC.

developed. The involvement of aryl cations in diazonium salt decomposition reactions has been the subject of considerable controversy.¹⁰ The understanding of the dediazonium process is complicated by the fact that its mechanism is not unique but is quite dependent on the reaction conditions. Dediazonium can occur by both ionic and free-radical paths.¹¹

Previous syntheses of aryl halides from arylamines have involved initial diazotization of arylamines followed by decomposition of the diazonium salt in the presence of a halide ion or a halogen radical source.^{4,8,9} Although satisfactory yields of aryl halides are usually obtained, these reactions are complicated by numerous competing reactions (Scheme I). Recently, numerous attempts have been made to gain control of side reactions. For example, decomposition of diazonium salts in nonpolar organic media has been conclusively demonstrated to generate aryl radicals,¹² and satisfactory yields of aryl halides could be obtained by using polyhalogenomethanes as a halogen source.⁸ However, aryl radicals abstract halogen from polyhalogenomethanes with variable efficiency,^{4,7,13} which limits the synthetic importance of the reaction. The recent successful uses of trimethylsilyl bromide and trimethylsilyl iodide as, inter alia, ether, ester, and 1,3-dioxolane cleavage reagents¹⁴ prompted us to investigate the decomposition

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