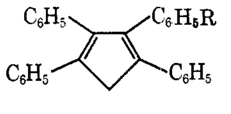
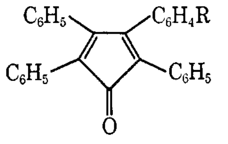
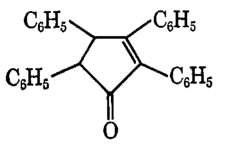
borohydride in ethanol solution at room temperature. Using an equimolar amount of borohydride, the purple color of ketone **2** was discharged only after 10 min; work-up at this stage afforded the enone **5**[5] in 34% yield. Infrared monitoring of a similar reduction showed the persistence of carbonyl absorption even after 20 hr of reaction time. On the other hand, use of a large excess of borohydride (5 mol equiv) led to the disappearance of all carbonyl absorption after 1 hr of reduction time. Work-up afforded an inseparable mixture of alcohols which could be dehydrated cleanly by treatment with iodine in refluxing benzene to give diene **1** in an overall yield of 55% from **2**.



1, R = H
4, R = *p*-OCH$_3$



2, R = H
3, R = *p*-OCH$_3$



5

Experimental Section[8]

1,2,3,4-Tetraphenylcyclopentadiene (1) from Tetracyclone (2). A. By Lithium Aluminum Hydride–Aluminum Chloride Reduction.—To a stirred solution of ketone **2** (0.384 g, 1 mmol) in dry ether (20 ml) was added aluminum chloride (0.266 g, 2 mmol), followed by lithium aluminum hydride (0.076 g, 2 mmol). After refluxing for 7 hr, excess hydride was decomposed by the addition of dilute hydrochloric acid. Evaporation of the dried (MgSO$_4$) ether solution left a residue of crystalline diene **1** (0.0352 g, 93%), mp 174–176°. Recrystallization from hexane afforded pure **1** (0.178 g) as first-crop fluffy needles, mp 180–182° (lit.[5] mp 180°); its qualitative ultraviolet spectrum was in accord with reported values.[5]

B. By Sodium Borohydride Reduction and Subsequent Dehydration.—Sodium borohydride (0.500 g, 13 mmol) was added at room temperature to a stirred solution of ketone **2** (1.00 g, 2.6 mmol) in ethanol (50 ml). After 1 hr, infrared monitoring of an aliquot showed the disappearance of carbonyl absorption and the development of a strong hydroxyl band at 2.8 μ. The solvent was evaporated *in vacuo*, the residue was treated with dilute hydrochloric acid, and the organic product (a complex mixture by tlc) was extracted into ether. The washed (aqueous NaHCO$_3$) and dried (MgSO$_4$) extract was evaporated, and the residue (0.91 g) was dissolved in benzene (50 ml). Iodine (0.100 g) was added and the solution was refluxed for 1 hr, after which the solution was cooled and shaken with aqueous NaHSO$_3$ to reduce the iodine. Evaporation of the dried solution, followed by crystallization from ethanol, yielded diene **1** (0.55 g), mp 180–182°.

2-(*p*-Methoxyphenyl)-1,3,4-triphenylcyclopentadiene (4).—3-(*p*-Methoxyphenyl)-2,4,5-triphenylcyclopentadienone (**3**, 0.103 g, 0.25 mmol)[6] was reduced as described above (method A for **1** from **2**), using aluminum chloride (0.133 g, 1 mmol) and lithium aluminum hydride (0.038 g, 1 mmol) as the reagents. The crude crystalline diene **4** (0.090 g) showed essentially one spot by tlc and no hydroxyl or carbonyl absorption in the infrared. Crystallization from hexane gave diene **4** (0.064 g, 64%) as needles, mp 128–130°. Recrystallization from hexane raised the mp to 132–133° (lit.[7] melting point 130–131°).

Registry No.—**1**, 15570-45-3; **2**, 479-33-4.

Acknowledgment.—Support of this work by the National Science Foundation (Grant GP-4931) is gratefully acknowledged.

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[8] Melting points are uncorrected and were determined using a Thomas-Hoover apparatus.

Photochlorination of Methylenecyclopropane

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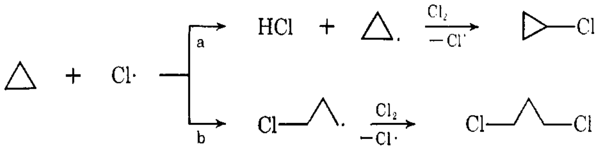
Received May 10, 1969

Photochlorination of cyclopropane[1] is a useful method for preparing chlorocyclopropane because abstraction of a cyclopropyl hydrogen by chlorine atom, a, to give hydrogen chloride and cyclopropyl free radical competes successfully with the simultaneous reaction, b, that gives 3-chloropropyl free radical.



Consider photochlorination of methylenecyclopropane (**1**). The greater strain in **1**,[2] which is relieved on ring opening, should cause b to occur more rapidly than with cyclopropane. Also, the exocyclic double bond of **1** can be expected to provide allylic-like resonance stabilization of the transition state for the substitution reaction,[4] but, because of orthogonality, similar stabilization of the transition state for the ring-opening reaction is not allowed. Therefore, it seems reasonable to expect that both reactions will occur more rapidly with **1** than with cyclopropane. However, prediction of the relative importance of these two pathways is uncertain.

We photochlorinated **1** in order to determine the relative importance of substitution and ring opening and, not incidentally, to see if the reaction might prove to be a convenient synthesis of 1-chloro-2-methylenecyclopropane (**2**). No **2** was obtained, but 3-chloro-2-chloromethyl-1-propene (**3**) was the major product. In addition, two other dichlorinated products, 1-chloro-1-chloromethylcyclopropane (**4**) and 2,4-dichloro-1-butene (**5**), as well as small amounts of products of further chlorination, 2-chloromethyl-1,3-dichloro-1-propene (**6**) and 2-chloromethyl-1,2,3-trichloropropane (**7**), were isolated and identified. The composition of these products from a typical reaction is summarized in Table I.

Formation of **3** and **4** can be explained as occurring by initial attack of chlorine atom at the double bond of

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(1) J. D. Roberts and P. H. Dirstine, *J. Amer. Chem. Soc.*, **67**, 1281 (1945).

(2) The strain energies of cyclopropane and methylenecyclopropane are 27.5 and 41.0 kcal/mole, respectively.[3]

(3) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968). See also: R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968); N. C. Baird and M. J. S. Dewar, *ibid.*, **89**, 3966 (1967); and H. A. Skinner and G. Pilcher, *Quart. Rev.* (London), **20**, 264 (1966).

(4) In deuterium oxide at 152°, 2-methylenecyclopropanecarboxylate undergoes deuterioxide-catalyzed exchange of its α hydrogen 10^6 times faster than cyclopropanecarboxylate.[5]

(5) A. T. Bottini and A. J. Davidson, *J. Org. Chem.*, **30**, 3302 (1965).

SCHEME I

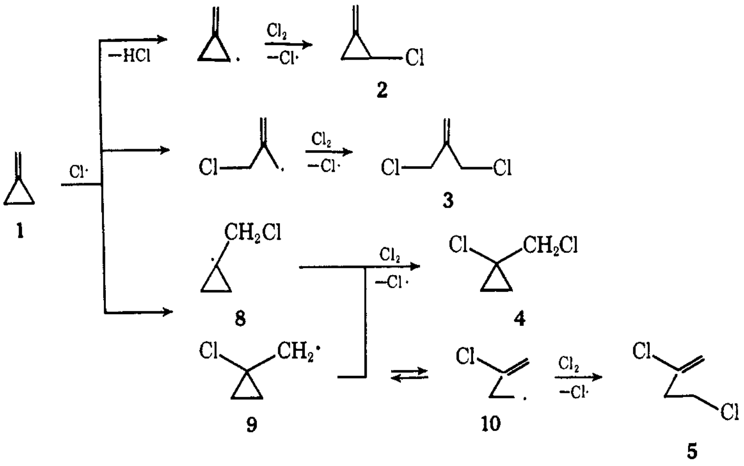


TABLE I

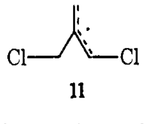
COMPOSITION OF PRODUCTS FROM PHOTOCHLORINATION OF 1-METHYLENECYCLOPROPANE[a]

Compound	Mol %[b]
3-Chloro-2-chloromethyl-1-propene (3)	42
1-Chloro-1-chloromethylcyclopropane (4)	18
2,4-Dichloro-1-butene (5)	27
2-Chloromethyl-1,3-dichloro-1-propene (6)	2
2-Chloromethyl-1,2,3-trichloropropane (7)	11

[a] Traces of two other products, too slow moving to be 2, were noted in gas–liquid phase chromatograms of this and another product mixture. A small amount of 2-methylallyl chloride, probably an artifact, was also present in reaction mixtures. [b] The total yield, not corrected for unreacted 1, was 34%.

1, which can give the free radicals 8 and 9. Significantly, photochlorination of methylcyclopropane[6] gives considerable allylcarbinyl chloride together with cyclopropylcarbinyl chloride and other products. Most likely, the former two products are formed *via* cyclopropylcarbinyl free radical, some of which rearranges to allylcarbinyl free radical before reacting with chlorine.[7] Note that similar behavior of 1-chlorocyclopropylcarbinyl free radical (9) gives 2-chloroallylcarbinyl free radical (10), which gives 5 on reaction with chlorine. Compound 4 could be formed by reaction of chlorine with 1-chloromethylcyclopropyl free radical (8) or 9. Interestingly, free radical addition of ethanethiol to 1 gives a 43% yield of ethyl cyclopropylcarbinyl thioether,[8] and this indicates that some 4 is indeed formed from 8. See Scheme I.

Conceivably, 11, the precursor of 6, could be formed by attack of chlorine atom on 2. Another way that 11 can be formed, and the one we believe to be the most important, is abstraction by chlorine atom of an allylic hydrogen from 3.



11

Failure to obtain 2 from photochlorination of 1 shows that the exocyclic double bond does not provide sufficient allylic-like stabilization to the transition state for substitution to allow that reaction to compete significantly with ring opening.

Experimental Section

Temperatures are uncorrected. Ir spectra were obtained of neat liquids with a Beckman IR-4 spectrophotometer. Nmr spectra were obtained of 20% solutions in CCl$_4$ at 60 MHz with a Varian Associates HR-60 system, equipped with V-3521 integrator and base-line stabilizer. Resonance frequencies in nmr spectra were determined relative to internal tetramethylsilane by the side-band technique. Glp chromatograms were obtained with a Loe Model 1 Chromat-O-Flex or a Wilkens Model A-700 gas chromatograph; the latter instrument was used for preparative glpc. Microanalyses were performed by the Microanalytical Laboratory, University of California, Berkeley.

Photochlorination of Methylenecyclopropane (1).—The apparatus used was similar to that described for the photochlorination of cyclobutane.[9] The exposed parts of the apparatus were covered with aluminum foil, except for the reaction chamber, which was illuminated with one or two 275-W GE sunlamps at a distance of 9 cm. The following reaction, in which two sunlamps were used, is typical. An 8.5-g sample (0.16 mol) of 95% pure 1[10] was placed in the boiler and heated with a silicone oil bath so as to maintain rapid reflux from the Dry Ice condenser. After several minutes, chlorine was admitted to the system at a rate of *ca.* 250 ml/hr. During the reaction, the bath temperature was raised gradually from 11° to maintain rapid reflux; after 6 hr, when the reaction was stopped, the temperature in the boiler had risen to 80°. The contents of the boiler were distilled through a semi-micro Claisen head and two fractions collected. The first, bp 70–140°, weighed 6.1 g, and the second, bp 80–120° (30 mm), weighed 1.4 g.

Separation and Identification of Photochlorination Products.—Glpc on XF-1150 at 95° with a helium flow rate of 150 ml/min allowed separation of the lower-boiling fraction into its components. Compounds 3, 4, and 5 had retention times of 16.3, 13.0, and 9.3 min, respectively. Glpc on didecyl phthalate at 160° with a helium flow rate of 60 ml/min showed that the higher boiling fraction contained small amounts of 3–5 together with 6 and 7. The latter two compounds had retention times of 7.3 and 15.3 min, respectively. Samples of 3–7 were obtained by preparative glpc. The 6 obtained was 95% pure, and the other samples were >98% pure by glpc. Relative responses of the components, which were determined by examination of chromatograms of prepared mixtures, allowed estimation of the composition of the product mixture, and this estimation is given in Table I. The mixture obtained from another reaction was also analyzed carefully. The mole per cents of 3–7 in the mixture were 35, 11, 18, 7, and 29, respectively, and the uncorrected yield was 32%.

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(6) E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 1987 (1961).

(7) Interconversion of cyclopropylcarbinyl and allylcarbinyl free radicals is well documented. See L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 934, 3050, 6556 (1967); L. K. Montgomery, J. W. Matt, and J. R. Webster, *ibid.*, **89**, 923 (1967); T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *ibid.*, **89**, 3051 (1967).

(8) B. C. Anderson, *J. Org. Chem.*, **27**, 2720 (1962).

(9) J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951).

(10) Analyzed using a 200 × 0.04 cm column packed with 20% adiponitrile on 60–80 mesh firebrick at 0° with a helium flow rate of 0.4 ml/min. We wish to thank Professor R. K. Brinton for his help in these analyses.

3-Chloro-2-chloromethyl-1-propene (**3**) was identified by comparison of its ir and nmr spectra with those of the starting material used for preparing **1**.

1-Chloro-1-chloromethylcyclopropane (**4**), $n^{26}\text{D}$ 1.4665, was identified by means of its ir spectrum, which is markedly similar to that of 1-bromo-1-bromomethylcyclopropane,[8] except that it does not have a band at 1110 cm^{-1} but does have one at 1250 cm^{-1}. A noteworthy feature of the ir spectrum of **4** is the relatively low intensity of the bands in the C–H stretching region (2500–3100 cm^{-1}).[11] The nmr spectrum, δ 3.74 (s, 2), 1.02–1.25 (m, 4), is also consistent with the assigned structure. Compound **4** rapidly gave a precipitate when treated with alcoholic silver nitrate at room temperature.

Anal. Calcd for $C_4H_6Cl_2$: C, 38.43; H, 4.84; Cl, 56.73. Found: C, 38.15; H, 5.23; Cl, 56.68.

2,4-Dichloro-1-butene (**5**), $n^{26}\text{D}$ 1.4595, was identified by means of its nmr spectrum: 5.28 (s, 2), 3.64 (t, J = 6.9 Hz, 2), 2.74 (t, J = 6.9 Hz, 2). Compound **5** gave only slight turbidity when treated with alcoholic silver nitrate at room temperature.

Anal. Calcd for $C_4H_6Cl_2$: C, 38.43; H, 4.84; Cl, 56.73. Found: C, 38.19; H, 5.30; Cl, 57.04.

2-Chloromethyl-1,3-dichloro-1-propene (**6**), lit.[13] bp 62–64° (9 mm), and 2-chloromethyl-1,2,3-trichloropropane (**7**), lit.[11] bp 87° (15 mm), were also identified by means of their nmr spectra. The spectrum of **6** consists of narrow multiplets at δ 6.38 (1), 4.35 (2), and 4.20 (2); that of **7** is a singlet at δ 3.90.

Registry No.—**1,** 6142-73-0.

(11) *Cf.* J. D. Roberts and V. C. Chambers, Jr., *J. Amer. Chem. Soc.*, **73**, 5030 (1951).

(12) H. Kleinfeller, *Chem. Ber.*, **62B**, 1586 (1929).

(13) R. W. Taft, Jr. and G. W. Stratton, *Ind. Eng. Chem.*, **40**, 1485 (1948).

Preparation and Irradiation of Spiro[2,3-benzonorbornadiene-7,1′-cyclopropane]

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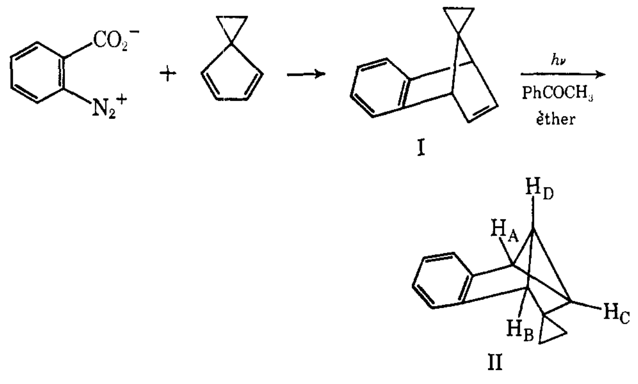
Received May 10, 1969

In order to study the effect of cyclopropyl conjugation on the photochemical isomerization of divinyl methane systems, we investigated the direct and sensitized irradiations of spiro[2,3-benzonorbornadiene-7,1′-cyclopropane] (I).[1] This compound was prepared in 63% yield by the addition of benzyne to spiro[4,2-hepta-1,3-diene].



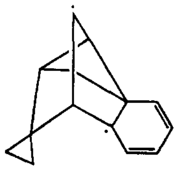
I

II

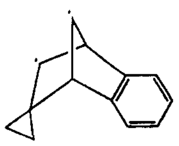
Irradiation of a 1% solution of I in ether at 2537 Å for 48 hr led to almost complete recovery of starting material, only a trace amount of a second unidentified component, and a trace amount of photoproduct II. Irradiation of a 1% solution of I in ether containing 0.01% acetophenone at 3500 Å for 48 hr produced only a 65% conversion of starting material to a photoisomer (II). The structure was established by spectral data. Mass spectral data indicated a molecular formula of $C_{13}H_{12}$ and showed peaks at m/e 128 (naphthalene radical cation) and 115 (indenium cation). The nmr clearly defined the structure. It shows a complex aromatic region for 4 H centered at 6.9 ppm. The hydrogens of the spiro cyclopropane ring are a complex multiplet centered at 0.7 ppm (3 H) and −0.3 ppm (1 H). The absorptions for the ring protons of the bicyclic system were analyzed by spin decoupling techniques. H_A appeared at 3.47 ppm and was coupled to H_B (2.5 Hz), H_C (5.0 Hz), and H_D (5.0 Hz). H_B appeared at 2.90 ppm and in addition to coupling with H_A was coupled to H_D (2.5 Hz). H_C, coupling to both H_A (5 Hz) and H_D (5 Hz), appeared at 2.49 ppm. Finally, H_D, coupled to the three other hydrogens, appeared at 1.74 ppm. The chemical shifts are comparable to the absorptions for the benzonorbornadiene photoproduct although the assignments in the latter case must be adjusted.[2]

The above results indicate that the cyclopropane ring has no effect on the course of the reaction although it has a dramatic effect on the rate of the reaction. Whereas the reaction of benzonorbornadiene is 95% complete in 24 hr, under identical conditions, I rearranged only to the extent of about 45%. Both reactions are triplet as indicated by the requirement of acetophenone sensitizations.

Several explanations may account for the rate decrease. First, the steric effect of the cyclopropyl group may decrease the rate of triplet energy transfer. If it is assumed that the sensitizer must approach the *exo* face of the benzene ring of benzonorbornadiene for energy transfer, placement of *gem* substituents at the 7 position (*i.e.* the cyclopropane ring) would hinder that approach. Triplet triplet energy transfer requires close approach of the two interacting molecules.[3] Second, the cyclopropane ring may promote the demotion of the excited state to ground state in some unknown manner. It is highly unlikely that cyclopropyl interaction with the presumed intermediate diradicals III or IV would lead to this result.



III



IV

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(1) (a) R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967); (b) J. Meinwald and G. W. Smith, *ibid.*, **89**, 4923 (1967); (c) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6069 (1968).

(2) J. R. Edman, *ibid.*, **88**, 3454 (1966).

(3) (a) D. L. Dexter, *J. Chem. Phys.*, **21**, 1836 (1953); (b) V. L. Ermolaev, *Opt. Spectrosc.* (USSR) **6**, 417 (1959); (c) V. L. Ermolaev, *Soviet Phys.-Usp.*, **6**, 333 (1963).