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**), $n^{26}D$ 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**), $n^{26}D$ 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.[12] bp 62–64° (9 mm), and 2-chloromethyl-1,2,3-trichloropropane (**7**), lit.[13] 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).
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Preparation and Irradiation of Spiro[2,3-benzonorbornadiene-7,1′-cyclopropane]

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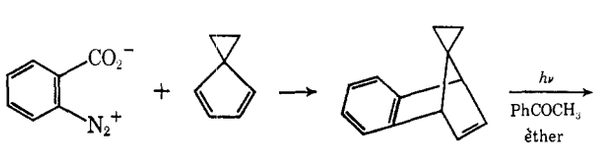
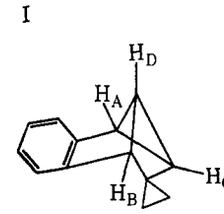
In order to study the effect of cyclopropyl conjugation on the photochemical isomerization of divinyl methane systems, we investigated the direct and sensitized irradiations of spiro[2,3-benzonorbornadiene-7,1′-cyclopropane] (I).[1] This compound was prepared in 63% yield by the addition of benzyne to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



I

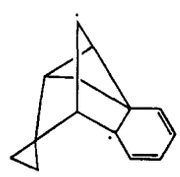


II

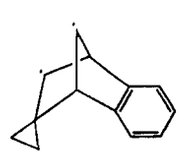
Irradiation of a 1% solution of I in ether at 2537 Å for 48 hr led to almost complete recovery of starting material, only a trace amount of a second unidentified component, and a trace amount of photoproduct II. Irradiation of a 1% solution of I in ether containing 0.01% acetophenone at 3500 Å for 48 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

(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).

Experimental Section[4]

Preparation of Spiro[2,3-benzonorbornadiene-7,1′-cyclopropane].—To a stirred solution of 6.50 g (55 mmol) of isoamyl nitrite in 80 ml of methylene chloride was added 4.6 g (50 mmol) of spiro[4,2-hepta-1,3-diene].[5] After bringing the solution to reflux, a solution of 7.55 g (55 mmol) of anthranilic acid in 40 ml of anhydrous acetone was added dropwise over 1.5 hr. The reflux was maintained an additional 15 min and then the solvents removed *in vacuo*. The residue was dissolved in pentane and washed with 10% aqueous sodium hydroxide solution. After drying and removal of solvent, an oil remained whose nmr indicated it was virtually pure. Distillation at 45° (0.1 mm) produced a slightly yellow solid, 5.25 g (63% yield), mp 32–35°. Recrystallization from methanol gave colorless needles, mp 36–39°. A sample collected from vpc[6] had mp 40–42°. The nmr spectrum showed a multiplet at 6.70–7.20 ppm (6 H), a triplet (J = 1.5 Hz) for 2 H at 3.18 ppm, and a multiplet for 4 H centered at 0.51 ppm. *Anal.* Calcd for $C_{13}H_{12}$: mol wt, 168.0938. Found: mol wt, 168.0933.

Irradiation of Spiro[2,3-benzonorbornadiene-7,1′-cyclopropane].—A solution of 200 mg (1.12 mmol) of I in 20 ml of dry degassed ether containing 2.0 mg of acetophenone was irradiated in a Srinivasan–Griffin photochemical reactor fitted with 3500-Å lamps. Following the reaction by thin layer[7] and vpc[6] revealed about 45% reaction after 24 hr and 65% reaction after 48 hr. After 48 hr, the irradiation was discontinued, solvent evaporated, and the product isolated after three successive elutions with Skelly B on 1-mm preparative thin layer plates. In this way 60 mg (30% recovery) of starting material and 110 mg (55% yield) of photoproduct II were obtained. The nmr and mass spectra have already been reported (*vide supra*). *Anal.* Calcd for $C_{13}H_{12}$: mol wt, 168.0938. Found: mol wt, 168.0929.

Registry No.—I, 22003-58-3; II, 22003-59-4.

Acknowledgment.—We wish to express our thanks to the National Institutes of Health and the Alfred P. Sloan Foundation for support of this work. We wish to thank R. W. LaRochelle for a sample of spiro[4.2-hepta-1,3-diene].

(4) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Beckmann IR 8 infrared recording spectrophotometer fitted with a grating. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 15. The nmr spectra were determined at 60 Mc with a Varian, Model A-60A nmr spectrometer. The mass spectra were obtained with a AEI MS-9 mass spectrometer.

(5) C. F. Wilcox, Jr., and R. B. Craig, *J. Amer. Chem. Soc.*, **83**, 3866 (1961).

(6) Vpc analysis performed on 8 ft × 0.25 in. 20% silicone oil 710 on Chromosorb P column.

(7) Thin layer chromatographic analyses and separations employed silica gel PF 254.

Structure and Reactivity in Intramolecular Aldol Condensations of *cis*-Disubstituted Cyclopropanes

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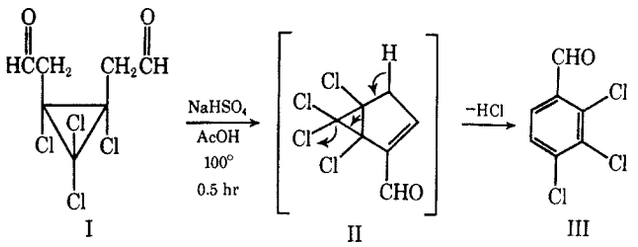
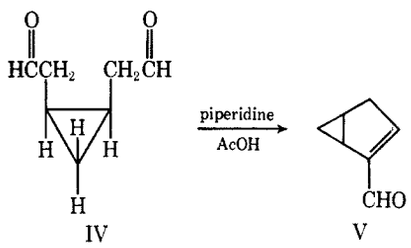
Our interest in intramolecular aldol condensations originated with the observation of the facile cyclization of 1,2,3,3-tetrachlorocyclopropane-*cis*-1,2-diacetaldehyde (I) to 2,3,4-trichlorobenzaldehyde[1] (III). Intermediate II was not isolated but is assumed to be a logical step on the way to the aromatic system, especially in view of the reported isolation of a similar condensation product, V, from the nonchlorinated analog, cyclopropane-*cis*-1,2-diacetaldehyde[2] (IV).



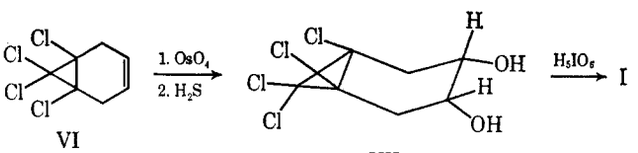
I II III



IV V

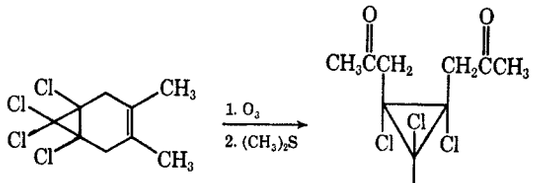
The two side chains on these cyclopropanes are *cis* and thus are in favorable position for aldol condensation. Dialdehyde I could not be obtained in crystalline form, so the analogous dimethyl ketone was synthesized and obtained as a crystalline product. It was found to undergo a similar rearrangement to 2,3,4-trichloro-6-methylacetophenone, and its crystal structure was determined to learn the extent of interaction between the acetone side chains in the ground state. The X-ray crystal structure, which is mentioned later in this paper, will be discussed in detail elsewhere.[3]

Oxidation of 1,6,7,7-tetrachloro-*cis*-bicyclo[4.1.0]-hept-3-ene (VI) with osmium tetroxide–pyridine complex gave the *cis*-diol VII, which was cleaved with periodic acid to dialdehyde I. Rearrangement of I to aldehyde III was complete in 0.5 hr in 82% overall yield from glycol VII.



VI VII

Synthesis of the diketone IX was accomplished as shown by oxidation of the Diels–Alder adduct (VIII) of tetrachlorocyclopropene and 2,3-dimethylbutadiene, using the method of Pappas, *et al.*[4]



VIII IX

(1) J. K. Hecht, *Tetrahedron Lett.*, 3503 (1968).

(2) F. Serratosa and E. Solé, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **63**, 865 (1967).

(3) F. P. Boer, J. J. Flynn, Jr., and J. K. Hecht, to be published.

(4) J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Lett.*, 4273 (1966).