was added dropwise at 0°, with stirring. After stirring at 0° for 5 min., the solution was allowed to warm to room temperature, and the silver salts and silver metal were filtered off. Acidification of the filtrate and extraction with ether gave, after removal of the ether under reduced pressure, 0.49 g. (90%) of pale yellow oil, $n^{20}\mathrm{D}$ 1.5412. The infrared spectrum was identical with that of the *trans* isomer described above except in the 1230–1260 cm.$^{-1}$ region where the *cis* compound had two bands of approximately equal intensity at 1232 and 1256 cm.$^{-1}$ while the *trans* isomer had a somewhat stronger band at 1236 cm.$^{-1}$ with a shoulder at 1255 cm.$^{-1}$. This difference appeared in several preparations of each compound. The amide prepared from 0.21 g. (0.0011 mole) of the acid by the method employed for the *trans*-amide was obtained as 0.18 g. (86% yield), m.p. 155.5–157°. Recrystallization from ethylene chloride gave 0.12 g. of *cis*-amide, m.p. 158–158.5°. The m.p. was not changed by further recrystallization. A mixed m.p. with the *trans*-amide was 151.5–154°.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.2; H, 8.0; N, 7.4. Found: C, 76.2; H, 8.0; N, 7.4.

Conversion of *cis*(?)-and *trans*(?)-3-Phenylcyclopentanecarboxylic Acid to 3,4-Benz-2-ketobicyclo[3.2.1]octane (IX).—A mixture of the cyclopentanecarboxylic acid and polyphosphoric acid was stirred intermittently at room temperature for 3 hr. and then on a steam-bath for 1–1.5 hr. The reaction mixture was then poured into 100 ml. of ice-water and extracted with ether. The ether solution was extracted with 10% sodium carbonate to remove any unreacted acid and, after drying, the solvent was distilled off under reduced pressure. From 1.4 g. (0.0074 mole) of *trans*-carboxylic acid and 16 g. of polyphosphoric acid was obtained 0.99 g. (78%) of IX as a light red oil, $n^{25}\mathrm{D}$ 1.5798 (reported[34] 1.577). From 0.52 g. (0.0027 mole) of *cis*-acid and 7.7 g. of polyphosphoric acid was obtained 0.40 g. (85%) of red IX, $n^{25}\mathrm{D}$ 1.5791. In each case the infrared spectra had strong carbonyl stretching absorption at 1692 cm.$^{-1}$. The spectrum of the sample from the *cis*-acid differed from that of the *trans* only by a weak band at 1775 cm.$^{-1}$. In each case the 2,4-dinitrophenylhydrazone recrystallized from dioxane had m.p. 250.5–251.5° (reported[34] 248–249°).

URBANA, ILL.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

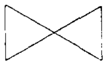
Chemistry of Spiropentane. II. The Chlorination of Spiropentane

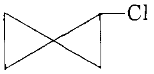
BY DOUGLAS E. APPLEQUIST, GEORGE F. FANTA AND BERTEL W. HENRIKSON

RECEIVED SEPTEMBER 14, 1959

The product mixture obtained by free-radical chlorination of spiropentane has been shown to consist in part of the normal substitution product, chlorospiropentane, but mainly of chlorides which can be accounted for by initial ring-opening attack of a chlorine atom on carbon. The latter products include 1,1-bis-(chloromethyl)-cyclopropane, 4-chloro-2-chloromethyl-1-butene and 1,2,4-trichloro-2-chloromethylbutane.

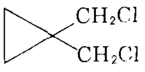
Although spiropentane(I) has been known for a number of years,[1] no substituted spiropentanes are known except the perdeuterated spiropentane.[2] Since the standard preparation of spiropentane by dehalogenation of pentaerythrityl tetrahalides is not readily extended to the synthesis of spiropentane derivatives, a promising approach to the preparation of such derivatives appeared to be direct free-radical substitution reactions on spiropentane, analogous to the reported successful chlorination[3] and nitration[4] of cyclopropane. This paper reports a study of the free-radical chlorination of spiropentane, a reaction expected to yield chlorospiropentane (II), which was desired for an investigation to be described in a future publication.


I

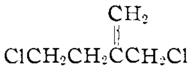


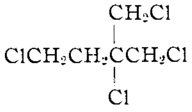
II

Photoinduced chlorination of spiropentane in the gas phase was studied with spiropentane to chlorine mole ratios of 10:1 to 30:1 with provision for removing chlorinated products as they formed. Distillation and gas chromatography of the reaction mixture revealed that there were four major products, which are here assigned the structures II–V.



III


$CH_2{=}C(CH_2Cl)CH_2CH_2Cl$
IV


$ClCH_2CH_2C(Cl)(CH_2Cl)CH_2Cl$
V

The structure of chlorospiropentane (II) was assigned on the basis of its analysis, its reduction to spiropentane with lithium in tetrahydrofuran followed by ethanol (78% yield) and by its n.m.r. and infrared spectra. The n.m.r. spectrum (60 mc.) showed a quartet of nearly equal signals centered at 1.48 p.p.m. from water and spaced 3 cycles apart, which was assigned to the hydrogen α to the chlorine. There was a triplet (areas approximately 1:2:1, with the central signal nearly resolved into two) at 3.38 p.p.m., spaced 6 cycles apart, which was assigned to one of the β-hydrogens; and there was a quartet centered at 3.65 p.p.m., spaced successively 3,2 and 3 cycles apart, which was assigned to the other β-hydrogen. The foregoing signals constitute a typical first-order three-proton spectrum in which all three protons are different.[5] In the present case, the two α-β coupling constants are 3 and 6 c.p.s. and the β-β coupling constant is about 5 c.p.s. The methylenes of the unsubstituted ring were represented by a strong signal at 3.82 p.p.m., with shoulders partially resolved on each side. The quartets for the β-hydrogens were found to be partially superimposed at 40 mc., making interpretation difficult. Spiropentane itself showed a single sharp signal at 4.04 p.p.m. The infrared spectrum of chlorospiropentane showed no C=C absorption, and contained

---

[1] D. E. Applequist, G. F. Fanta and B. W. Henrikson, *J. Org. Chem.*, **23**, 1715 (1958), and references cited therein.

[2] H. O. House, R. C. Lord and H. S. Rao, *ibid.*, **21**, 1487 (1956).

[3] J. D. Roberts and P. H. Dirstine, THIS JOURNAL, **67**, 1281 (1945).

[4] H. B. Hass and H. Shechter, *ibid.*, **75**, 1382 (1953).

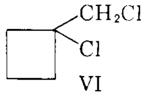
[5] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 130.

all of the peaks found in the spectrum of spiropentane.

The structure of 1,1-bis-(chloromethyl)-cyclopropane (III) was indicated by its n.m.r. spectrum (40 mc.), which showed two equal, unsplit signals at 1.15 and 4.04 p.p.m.; by the infrared spectrum, which showed no double-bond absorption and resembled strikingly the spectrum of 1,1-bis-(bromomethyl)-cyclopropane[6]; by its failure to react with neutral permanganate; and by its inertness to powdered potassium hydroxide, which was in fact used to isolate III in pure form.

The unsaturated dichloride IV gave a positive permanganate test and showed infrared absorption at 1642 cm.$^{-1}$. Its n.m.r. spectrum (40 mc.) showed two barely unresolved olefinic proton signals at -0.51 and -0.31 p.p.m., an unsplit peak at 0.71 p.p.m. due to the allylic $-CH_2Cl$, a triplet at 1.13 p.p.m. (separated about 6 c.p.s.) due to the other $-CH_2Cl$, and a triplet at 2.12 p.p.m. (separated about 7 c.p.s.) due to the remaining allylic $-CH_2-$.

The structures of III and IV were futher confirmed by demonstration of their anionotropic relationship through zinc chloride-catalyzed isomerization. A mixture of 10.2% IV and 86.2% III upon treatment with solid zinc chloride for 100 hr. at room temperature isomerized to a mixture containing 31.8% IV, 7.3% III and 58.6% of a new substance assigned the expected[6] structure VI. The n.m.r. spectrum (40 mc.) of the new compound was in agreement with structure VI, showing a sharp signal for $-CH_2Cl$ at 0.99 p.p.m. and a complex pattern for the ring methylenes at 2.0–3.1 p.p.m. Compound VI was also found among the products of chlorination of spiropentane to the extent of about 1%, but it may have arisen in whole or in part from methylenecyclobutane which was known to contaminate the spiropentane.



VI

The tetrachloro compound V was identified by its reduction with lithium aluminum hydride to a mixture of 2-methylbutane and 2-methyl-1-butene; by its infrared spectrum, which showed no C=C or C–CH$_3$ absorptions; and by its n.m.r. spectrum (40 mc.), which showed unsplit (0.83 p.p.m.) and triplet (0.95 p.p.m., $J \simeq 7.5$ c.p.s.) signals for $-CH_2Cl$ and a triplet (2.27 p.p.m., $J \simeq 7.5$ c.p.s.) for the remaining methylene.

It was found that the products II–V were obtained in different proportions, depending upon the temperature and intensity of irradiation. It was found, in fact, that the same products were obtained by a purely thermal chlorination (reaction D), although the reaction was slower. The product compositions from the various vapor-phase chlorinations are summarized in Table I. An attempt was made to make the reaction temperatures identical in runs C and D, but it is probable that the temperature in the reaction zone in run C was higher due to the known tendency of chlorine to become warmer upon strong irradiation (Budde effect[7]). The runs A to D are therefore probably arranged in descending order of actual reaction temperature, and the variation in product composition is possibly to be ascribed to the temperature effect. Two effects are notable: (1) The formation of chlorospiropentane (II) is favored by strong irradiation (higher temperatures); and (2) the product of single ring opening (III) is favored with respect to double ring opening (IV and V) by lower temperatures.

TABLE I

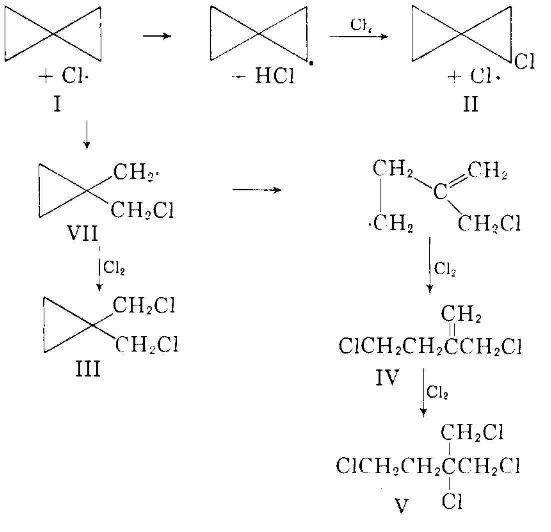
COMPOSITIONS OF PRODUCTS FROM VAPOR-PHASE CHLORINATION OF SPIROPENTANE

Experiment Conditions[a]	A[b] Two sunlamps, one heat lamp	B Two sunlamps	C One sunlamp	D Darkness, 116°
	Products, mole %			
II	43.2	43.2	36.2	9.6
III	3.8	8.8	25.1	63.4
IV	35.8	30.9	25.6	18.6
V	15.7	9.7	8.9	4.8
VI[c]	1.2	1.5	1.8	~1.2

[a] See Experimental for further details. [b] The spiropentane used in run A was only about 88% pure, being contaminated mainly by 2-methyl-1-butene. The product therefore contained at least eleven unidentified compounds, amounting to about 13.5% of the product mixture. The values shown in the table represent composition of the product mixture exclusive of these unidentified substances. [c] The spiropentane used in runs A–D contained about 1.6, 1.7, 0.7 and 0.1%, respectively, of methylenecyclobutane.

A mechanistic scheme which accounts for the foregoing observations is shown in Chart I. There appears to be no convenient explanation for the ring-opened products III–V except the attack of chlorine atom on carbon as shown. The ring opening of radical VII to yield completely open-chain products finds analogy in the formation of allylcarbinyl chloride by photochlorination of methylcyclopropane.[8]

Chart I



---

(6) D. E. Applequist and J. D. Roberts, THIS JOURNAL, **78**, 874 (1956).

(7) G. B. Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., Inc., (Reinhold Publ. Corp.), New York, N. Y., 1928, p. 138.

(8) J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951).

The free-radical displacement on carbon to form VII is a seldom observed class of reaction. In fact, there appear to be no thoroughly established examples of such displacements on tetrahedral carbons in open chains or unstrained rings, although some possible cases have been discovered and given preliminary examination.[9] On the other hand, it appears likely that free-radical displacements on cyclopropane carbon are more common, being quite well established in thermal iodine addition,[10] and by analogy probable for other halogen additions to cyclopropane.[3,11] The photosensitized polymerization of cyclopropane has been thought to proceed by a radical displacement on carbon,[12] but the more recently demonstrated complexity of the polymer makes such a conclusion dubious.[13] Free-radical additions to cyclopropanes are certainly less facile than additions to olefins, as shown by the relative unreactivity of cyclopropane toward halogens,[11] and by the failure of cyclopropyl cyanide, methyl cyclopropyl ketone and phenylcyclopropane to undergo radical-initiated polymerization.[12b]

The variation of product composition with intensity of illumination (Table I), if the effect is simply a temperature effect as assumed, is accounted for in terms of the mechanism of Chart I if the activation energy for hydrogen abstraction to form spiropentyl radical is higher than that of the ring opening to form VII, and if the activation energy for opening the second ring (in VII) is greater than that for formation of III from VII. The latter relationship appears reasonable, but the former is in contrast with the results of the thermal chlorination of cyclopropane,[3] where higher temperatures favored ring opening over substitution and temperatures over 500° were necessary to make ring opening a major reaction. A possible source of difference between spiropentane and cyclopropane is in the strain energies, but that of spiropentane (59 kcal.)[14] is only about twice that of cyclopropane (29 kcal.)[15] if the same, value of the C–C bond energy is used to obtain the empirical strains from the heats of combustion. (The figures shown were calculated using 82.4 kcal. as the C–C bond energy and 170.4 kcal. as the heat of sublimation of graphite.) If a larger value of the C–C bond energy is more appropriate for the hypothetical unstrained spiropentane, as seems reasonable in view of its branched structure,[16] then the strain in spiropentane would be more than twice that in cyclopropane, and the opening of the first ring by a chlorine atom would be facilitated.

Another effect which might contribute to the ease of ring opening of spiropentane is resonance stabilization (ionic or otherwise) of the transition state leading to VII, analogous to that which would account for the unusually fast decomposition of bis-cyclopropylacetyl peroxide.[17] It is difficult to see how such stabilization could be stereoelectronically favorable in the spiropentane ring opening, since the orbital which contains the odd electron in VII would be nearly orthogonal to the bent-bond orbitals of the undisturbed three-membered ring in the transition state for formation of VII.

As a further confirmation of the free-radical mechanism shown in Chart I, it has been shown that the products II–V are also formed in liquid phase chlorinations in sealed tubes, using excess spiropentane as solvent, and that the formation of all of these products in the liquid phase is strongly enhanced by light or by trichloroacetyl peroxide (which decomposes rapidly at room temperature). The yields, based on chlorine used, are shown in Table II. Several unidentified products were formed in these reactions even though the spiropentane was 97.5% pure or better, but such products would be expected in this situation where initial products are not removed from the reaction mixture. None of these extra products have been investigated further.

TABLE II

YIELDS OF PRODUCTS FROM LIQUID-PHASE CHLORINATION OF SPIROPENTANE

Experiment Conditions	E Total darkness, no peroxide, 24 hr.	F Total darkness peroxide, 4 hr.[a]	G Light 5 hr.
		Products, mole %	
	Products, mole %		
II	0.9	26	4
III	4	20	52
IV	0	18	2
V	0	5	7
VI	0	0	0
Unidentified	1.5	9	5

[a] Because of the speed at which trichloracetyl peroxide decomposes at room temperature, the reaction was probably complete in much less time, but darkness prevented visual observation of chlorine disappearance. See Experimental for details.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. We are indebted to Prof. Martin Saunders for a 60 mc. n.m.r. spectrum, to Mr. Ben Shoulders for the 40 mc. n.m.r. spectra, to Mr. Paul McMahon and Mrs. Mary Verkade for the infrared spectra, and to Mr. Josef Nemeth, Miss Claire Higham, Miss Jane Liu and Mrs. Ruby Ju for microanalyses.

Experimental[18]

Vapor-phase Chlorination of Spiropentane. Reaction C, One Sunlamp.—The chlorination apparatus was modeled

---

[9] (a) R. A. Herrmann and R. M. Noyes, THIS JOURNAL, **78**, 5764 (1956); (b) R. A. Holroyd and W. A. Noyes, Jr., *ibid.*, **76**, 1583 (1954); (c) H. G. Oswin, R. Rebbert and E. W. R. Steacie, *Can. J. Chem.*, **33**, 472 (1955).

[10] R. A. Ogg, Jr., and W. J. Priest, *J. Chem. Phys.*, **7**, 736 (1939).

[11] M. S. Kharasch, M. Z. Fineman and F. R. Mayo, THIS JOURNAL, **61**, 2139 (1939).

[12] (a) H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **17**, 351 (1949); (b) G. S. Hammond and R. W. Todd, THIS JOURNAL, **76**, 4081 (1954).

[13] K. J. Ivin, *J. Chem. Soc.*, 2241 (1956).

[14] F. M. Fraser and E. J. Prosen, *J. Research Natl. Bur. Standards*, **54**, 143 (1955).

[15] J. W. Knowlton and F. D. Rossini, *ibid.*, **43**, 113 (1949).

[16] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 274.

[17] H. Hart, J. M. Sandri and D. P. Wyman, Abstracts of the 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957, p. 65-O.

[18] Boiling points are uncorrected. Infrared spectra were measured with a Perkin-Elmer model 21B spectrophotometer with sodium chloride optics. Gas chromatography was done with a Perkin-Elmer model 154B vapor fractometer, using helium as the carrier gas.

after that used by Roberts and Mazur for the chlorination of cyclobutane.[8] The light source was a 275 w. sunlamp placed about 0.5 cm. from the glass spiral. Spiropentane[1] (27.3 g., 95.2% pure by vapor chromatography) was placed in the boiler and heated until the entire apparatus was filled with vapor as evidenced by rapid condensation at the Dry Ice condenser. Chlorine was then admitted to the system, the number of moles per minute being governed by a calibrated flow-meter. The ratio of chlorine to hydrocarbon was held at approximately 1:30 throughout the reaction. The reaction was stopped at the end of 6 hr. when the temperature of the liquid in the boiler reached 100°. Distillation of the crude reaction mixture through a 4.5-ft. modified Podbielniak column[19] yielded spiropentane (I) (b.p. 38.5°); spiropentyl chloride (II) (b.p. 93–99°); a mixture of III, IV and VI (b.p. 160–180°); and 1,2,4-trichloro-2-(chloromethyl)-butane (V) (b.p. 76.5–78° (2 mm.)). The mixture of III, IV and VI was analyzed by vapor chromatography (didecyl phthalate column) and the over-all mole percentages calculated using Eastmen's correction for molecular weights.[20] A sample of pure II was prepared by vapor chromatography. Molecular weights of unknown compounds present in low concentrations were estimated by their retention times with relation to known substances.

Anal. Calcd. for C_5H_7Cl (II): C, 58.54; H, 6.88. Found: C, 58.51; H, 7.11. Calcd. for $C_5H_8Cl_4$ (VI): C, 28.61; H, 3.84. Found: C, 28.68; H, 3.94.

Reaction B, Two Sunlamps.—The reaction with two 275 w. sunlamps placed approximately 1 cm. from the spiral[8] was similar to the above reaction, with the exception that the Dry Ice condenser was replaced by a spiral condenser cooled by an ice–brine mixture. The amount of spiropentane chlorinated was 18.8 g. (93% pure by vapor chromatography), and a 1:10 ratio of chlorine to hydrocarbon was maintained throughout the reaction. The reaction was stopped at the end of 7 hr. when the boiler temperature reached 100°. Spiropentane and spiropentyl chloride were removed by fractionation at atmospheric pressure though a 26-cm. spinning band column. The residue was analyzed by vapor chromatography at 154° (didecyl phthalate column) and the products identified by comparison of retention times with those of the products from the previous reaction.

Reaction A, Two Sunlamps and One Heat Lamp.—The procedure was like that in the above reactions but with two sunlamps about 1 and 2 cm. from the coil and a 250 w. heat lamp about 5 cm. from the coil. The lamps were covered with aluminum foil to maximize their efficiency. A Dry Ice condenser was used. Spiropentane amounting to 123 g. (approx. 88% pure) was chlorinated for 16.5 hr. at a 1:10 ratio of chlorine to hydrocarbon. The pot temperature was 100° at the end of this time. Gas chromatographic analysis (didecyl phthalate column) of the crude reaction mixture gave the data shown in Table I. This procedure was the best one for synthesis of chlorospiropentane (II), the isolated yield being 53 g. (b.p. 95–96°) (32%).

Reaction D, Total Darkness.—The apparatus for the dark reaction was identical with that used for reaction C. The glass spiral of the chlorination apparatus[8] was heated by means of a resistance wire heater to 116° (the approximate temperature measured for reaction C). The weight of spiropentane used was 16.3 g. (96.5% pure by vapor chromatography), and the chlorine to hydrocarbon ratio was maintained at 1:20 throughout the 6 hr. reaction time. At the end of this time, the boiler temperature was 65°. Thermometer and flowmeter readings were taken with the aid of a small penlight covered with several layers of red crepe paper. The reaction mixture was crudely fractionated in total darkness yielding 5.1 g. of low boiling material and 17.5 g. of high boiling residue. An infrared spectrum of the low boiling material was identical with that of a known sample of spiropentane. The over-all composition of the reaction mixture was determined by vapor chromatographic analyses of both low and high boiling materials (156°, didecyl phthalate column) and comparison of retention times with those of I through VI isolated from previous reactions.

Reduction of Spiropentyl Chloride (II).—In a micro 3-necked flask equipped with dropping funnel, stirrer and Dry Ice trap was placed a suspension of 0.24 g. (0.034 g. atom) of finely cut lithium wire in 4.5 ml. of tetrahydrofuran (THF) which had previously been distilled over lithium aluminum hydride. The contents of the flask were cooled to approximately −35°, and a solution of 1.4 g. (0.0136 mole) of spiropentyl chloride (98.4% pure by vapor chromatography) in 9.1 ml. of THF was then added over a two-hour period while the entire system was stirred and kept under an atmosphere of helium. After 23 hr. at −35 to −15°, the reaction mixture was decomposed by the addition of 5 ml. of absolute ethanol. The entire system was then swept with a slow stream of helium for 20 hr. to yield 6.37 g. of liquid in the Dry Ice trap. Analysis of this liquid by vapor chromatography (didecyl phthalate column) showed a low-boiling liquid to be present in addition to THF. A pure sample of this component was collected by vapor chromatography and was shown to have an infrared spectrum identical to that of spiropentane. The calculated yield of spiropentane was 78%.

Reduction of 1,2,4-Trichloro-2-(chloromethyl)-butane (V) with Lithium Aluminum Hydride.—To a micro side arm flask equipped with a water cooled reflux condenser which, in turn, was connected to a Dry Ice trap was added a suspension of 1.08 g. (0.0286 mole) of lithium aluminum hydride in 5 ml. of dry THF. After this mixture had been heated to reflux temperature, 1.00 g. (0.00477 mole) of V was added slowly from a hypodermic syringe mounted in the side arm of the flask. After addition of the chloride, the resulting mixture was held at reflux temperature for 2.5 hr. and allowed to cool overnight. The mixture was then again heated to reflux temperature and the system swept with helium for 2 hr. to yield 1.10 g. of liquid in the cold trap. The two major components of this mixture (excluding THF) were separated by means of vapor chromatography (didecyl phthalate column) and identified as 2-methylbutane (30% yield) and 2-methyl-1-butene (45% yield) by comparison of the infrared spectra with those of known compounds.[21]

Isomerization of Dichloride Mixture with Zinc Chloride and Isolation of 1-Chloro-1-chloromethylcyclobutane (VI).—A dichloride fraction containing 86.2% III, 10.2% IV, 2.2% VI and 1.5% of an unidentified substance was allowed to stand in the presence of anhydrous zinc chloride for 100 hr. From 0.576 g. of the mixture and 0.11 g. of zinc chloride was recovered, by distillation, 0.512 g. (89% recovery) of dichloride mixture which was analyzed by gas chromatography on a didecyl phthalate column. The product contained 7.34% III, 31.8% IV and 58.6% VI. From a similar reaction mixture, a high concentration of VI, b.p. 46–49° (11.3 mm.), was obtained by fractional distillation through a 26-cm. spinning-band column. Nearly pure VI was then isolated, contaminated with only traces of III and IV, by gas chromatography.

Anal. Calcd. for $C_5H_8Cl_2$: C, 43.19; H, 5.80. Found: C, 43.50; H, 5.74.

Treatment of Dichloride Mixture with Potassium Hydroxide and Isolation of 1,1-Bis-(chloromethyl)-cyclopropane (III).—To a micro reaction flask equipped with reflux condenser and calcium chloride tube was added 6.4 g. of a mixture containing approximately equimolar amounts of III and IV. Powdered potassium hydroxide (11.0 g.) was then added and the resulting mixture heated at steam-bath temperature for 7 hours. After cooling overnight, the mixture was diluted with diethyl ether and the excess potassium hydroxide removed by filtration. Ether was removed by distillation through a Holzman column, and the residue was then fractionated through a 26-cm. spinning band column to yield a total of 1.8 g. of colorless liquid, b.p. 48–51° (12.1 mm.). Vapor chromatography of a center fraction (didecylphthalate column) showed III to be 91.7% pure, IV being the only impurity. Infrared, n.m.r. and carbon-hydrogen analyses were obtained on this material.

Anal. Calcd. for $C_5H_8Cl_2$: C, 43.19; H, 5.80. Found: C, 43.35; H, 5.86.

Isolation of 4-Chloro-2-chloromethyl-1-butene (IV).—A sample of dichloride mixture, b.p. 68° (31 mm.), containing 80% IV was obtained by fractional distillation through the modified Podbielniak column. This sample was then distilled in part through a 26-cm. spinning-band column. The residue was found to be about 90% IV (gas chromatography), and was further purified by gas chromatography (didecyl

---

[19] J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 237.

[20] R. H. Eastman, THIS JOURNAL, **79**, 4243 (1957).

[21] American Petroleum Institute, Research Project 44 at National Bureau of Standards, "Infrared Absorption Spectrograms," Vol. I, Nos. 196, 241.

phthalate column) to give 99% IV containing 0.4% III and 0.6% of an unknown low boiling material which was easily removed by fractionation at reduced pressure through a semi-micro Vigreux column. Infrared, carbon-hydrogen and n.m.r. analyses were obtained on the material thus obtained.

Anal. Calcd. for $C_5H_8Cl_2$: C, 43.19; H, 5.80. Found: C, 43.39; H, 5.86.

Preparation of Trichloroacetyl Peroxide.—Trichloroacetyl peroxide was prepared in low yield by the method of Zimmerman[22] and used without recrystallization.

Liquid-phase Chlorination of Spiropentane. Reaction E, No Initiator.—To a small ampule with a constriction at the top to facilitate sealing was added 0.41 g. (0.00603 mole) of spiropentane of 99.4% purity. The resulting liquid was cooled to Dry Ice temperature, and 29.6 ml. (0.0014 mole) of gaseous chlorine was then slowly added by means of a gas buret through a capillary tube extending below the surface of the liquid. The addition of chlorine was made in total darkness. After addition was complete, the ampule was quickly sealed with an oxygen torch and allowed to stand at room temperature in total darkness for 24 hr. At the end of this time, the ampule was broken and the reaction mixture poured into a saturated solution of sodium bisulfite at 0°. After remaining in contact with the bisulfite solution for 10 min. to destroy all unreacted chlorine, the mixture was removed from the dark and the organic layer separated, dried and distilled. The mixture was analyzed by vapor chromatography at 156° (didecyl phthalate column), employing Eastman's correction for molecular weights.[20] The molecular weights of unknown compounds, which were present in small amounts in all three liquid phase reactions, were estimated by their retention times with relation to known compounds. Major products were identified by comparison of retention times with those of known samples of I, II and III. An infrared spectrum of the reaction mixture was identical with that of a known sample of spiropentane except for a weak absorption at 1265 cm.$^{-1}$ which may be attributed to the presence of III.

Reaction F, Initiation by Peroxide.—The same apparatus and procedure was used as was discussed for the uninitated case. The spiropentane used was of 97.5% purity and amounted to 0.88 g. (0.0129 mole). The impurities were all present in less than 0.4%, except 1,1-dimethylcyclopropane which was present in a concentration of 1.2% (determined by vapor chromatography).[1] After the ampule containing spiropentane had been cooled to Dry Ice temperature, approximately 10 mg. of trichloroacetyl peroxide was added. The peroxide could not be weighed due to its rapid, and sometimes violent decomposition at or near room temperature. Chlorine (62 ml., 0.0025 mole) was then added, as before, in total darkness. After sealing, the ampule was completely submerged in a beaker of water at room temperature and allowed to stand in total darkness for 4 hr. Any excess chlorine was again decomposed with bisulfite and the organic layer separated, dried and distilled. The reaction mixture was analyzed by vapor chromatography in a manner identical to that described for the reaction E, retention times being compared with those of known samples of I, II, III, IV and V. After removal of excess spiropentane, a crude distillation of the reaction mixture yielded three fractions. The infrared spectrum of fraction 1 clearly showed the presence of II. Similarly, infrared analysis of fraction 2 indicated a mixture of III and IV. Compound V was further identified by comparison of the vapor chromatographic retention time of this component in fraction 3 with a known sample at 190° (silicone oil column).

Reaction G, Initiation by Light.—The same apparatus and general procedure was used as was employed in the two previous liquid phase chlorinations. Chlorine (57.7 ml., 0.0023 mole) was added to 0.795 g. (0.0117 mole) of spiropentane of the same purity as that used for the peroxide-initiated reaction. The addition of chlorine and the sealing of the ampule were, as before, carried out in darkness. After submerging the sealed ampule in a beaker of water at room temperature, the contents of the beaker were irradiated with a 275 w. sunlamp for 1.5 hr. starting at a distance of 12 ft. and moving to 6 ft. at the end of 45 min. Since no noticeable reaction occurred with the lamp at these distances, the reaction mixture was irradiated at 3 ft. for a total of 3.5 hr. After 1 hr. at this distance, the reaction mixture was almost colorless. At the end of the 5 hr. reaction time, the colorless reaction mixture was treated with bisulfite, separated, dried and distilled as before. Analysis and identification of products by comparison of vapor chromatographic retention times with authentic samples at 156° was carried out as in the two previous reactions. Since the concentration of spiropentyl chloride was too low to permit isolation by distillation, the presence of II was further proved by comparison of its rentention time with that of a known sample at 132° (didecyl phthalate column). Infrared analysis of the above reaction mixture, after removal of excess spiropentane, clearly showed the presence of III and suggested the presence of IV. Final identification of V in the above concentrated reaction mixture was accomplished by comparison of its retention time with that of an authentic sample at 190° (silicone oil column).

Nuclear Magnetic Resonance Spectra.—The n.m.r. spectra were measured in carbon tetrachloride solution with a Varian high resolution spectrometer (model V-4300B with super stabilizer) using methylene chloride as an external standard. The 40 mc. spectra were measured in carbon tetrachloride solutions at the following concentrations for the various substances: I, 296 mg./ml.; II, 370 mg./ml; III, 284 mg./ml.; IV, 260 mg./ml.; V, 212 mg./ml.; and VI, 260 mg./ml. The signal of the methylene chloride external standard was assumed to be at −0.65 p.p.m. from water. The 60 mc. spectrum of III was measured on the neat liquid, but the chemical shifts assigned in the discussion are those measured on the above 40 mc. spectrum in carbon tetrachloride. Where peaks were obscured by overlap at the lower frequency, it was assumed that relative shifts were the same in the two cases.

URBANA, ILL.

---

[22] C. Zimmerman, U. S. Patent 2,580,373 (1951); *C. A.*, **46**, P 6668a (1952).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of the Hunsdiecker Reaction on a Cyclopropane Ring[1]

BY DOUGLAS E. APPLEQUIST AND ALAN H. PETERSON

RECEIVED SEPTEMBER 21, 1959

The brominative decarboxylation (Hunsdiecker reaction) of silver 2-methylcyclopropanecarboxylate in carbon tetrachloride at room temperature has been found to give the same mixture of *cis*- and *trans*-2-methylcyclopropyl bromides from either the *cis* or *trans* silver salt. It is concluded that the cyclopropyl free radical is either planar about the 1-position or inverts its configuration very rapidly, and is thus qualitatively like an unstrained alkyl free radical.

Although extensive physical[2] and chemical[3] data have revealed that ordinary free alkyl radicals are either planar in configuration about the trivalent carbon or subject to rapid inversion if they are non-planar, very little attention has been given to the effect of hybridization changes on the stereo-

---

[1] Taken from the Ph.D. thesis of Alan H. Peterson, University of Illinois, 1960.

[2] (a) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956); (b) M. Karplus, *J. Chem. Phys.*, **30**, 15 (1959).

[3] (a) E. L. Eliel in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 140; (b) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 502.