The Reaction of 1-Phenyl-2-alkylcyclopropanes with N-Bromosuccinimide[1]

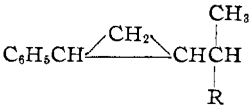
By Henry G. Kuivila, Stanley C. Caywood, Walter F. Boyce and Frederick L. Langevin, Jr.

Received May 27, 1955

The similarities between the cyclopropane ring and the double bond have been recognized for many years.[2] These have been revealed in the methods of preparation, addition reactions, ultraviolet absorption spectra and dipole moments. The spectral data indicate conjugation between the cyclopropane ring and double bonds. The extent of this conjugation is limited, however. This is shown by the work of Eastman[3] whose results on cyclopropyl ketones indicate that the ring can extend the chain of conjugation but cannot transmit conjugative effects. Similarly, 2-phenylbicyclopropyl shows no conjugation including both of the cyclopropane rings as revealed by spectroscopic studies by Smith and Rogier.[4]

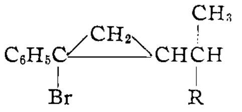
Several investigators have carried out reactions with cyclopropane derivatives in which free radicals are probably involved. In accord with the I-strain hypothesis of Brown,[5] cyclopropyl free radicals are difficult to produce. This is indicated by chlorination in the methyl group of methylcyclopropane,[6] slow reaction with methyl radicals and inertness to radicals formed in the decomposition of benzoyl peroxide, acetyl peroxide, bis-azodiethylacetonitrile and polymerizing styrene.[7] However, photochemical substitution by chlorine has been effected.[8] Atomic bromine[9] and iodine[10] both appear to open the cyclopropane ring with the formation of dihalides.

In an attempt to examine the relative characteristics of the cyclopropane ring with regard to conjugation and substitution by radicals we have investigated the reactions of 1-phenyl-2-ethylcyclopropane (I) and 1-phenyl-2-isopropylcyclopropane (II) with N-bromosuccinimide. Although the mechanisms of the Wohl–Ziegler reaction[11] have not been elucidated, it appears to be very probable that the peroxide and light-induced reactions at least proceed by free radical mechanism. It appeared possible that the reaction of N-bromosuccinimide with I and II would proceed by either of two paths. First, replacement of hydrogen on the 1-carbon of the cyclopropane ring analogous to the reaction with toluene to give III might occur. Alternatively, if this reaction were too slow, substitution might occur on the carbon of the alkyl group attached to the cyclopropane ring, giving IV as product. This could result from activation by the cyclopropane ring itself or by transmission of the activating effect of the benzene ring.

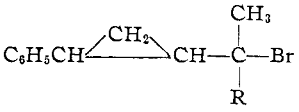


I, R = H

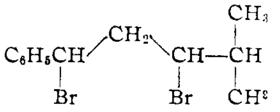
II, R = CH_3



III



IV



V

Preliminary experiments showed that II does not react with N-bromosuccinimide in refluxing carbon tetrachloride unless benzoyl peroxide is present. When molar equivalents of the succinimide and cyclopropane are used, one-half of the latter can be recovered so that two moles of succinimide were used in all subsequent experiments. The product could not be distilled at 1 mm. but could be purified by adsorption on alumina yielding 57% of a dibromide which proved to be a monomeric product of the addition of two bromine atoms to the hydrocarbon. The dibromide was dehydrobrominated with alcoholic silver nitrate to produce a diene with the same ultraviolet absorption spectrum, boiling point and refractive index as authentic 1-phenyl-4-methyl-1,3-pentadiene. The identity was confirmed by the preparation of identical tetrabromo derivatives from the two dienes.

The structure of the diene indicates that ring opening occurs between the two substituted carbons. This is in contrast with ring opening by hydrogen bromide, for example, which has been shown by Kohler and Conant[12] to take place between the most and least highly substituted carbons, Markownikoff's rule describing the direction of addition. The actual location of the bromine atoms in the addition product was not ascertained but may be inferred by the principle of minimum structural change to be as shown in structure V. There appears to be no reason to expect rearrangement of the dibromide under the conditions of the reaction or the dehydrobromination.

Treatment of 1-phenyl-2-ethylcyclopropane with N-bromosuccinimide in the presence of benzoyl peroxide yielded 23% of a dibromide. The same product was obtained by treatment of the hydrocarbon with bromine in carbon tetrachloride at room temperature. No diene was formed when it was treated with alcoholic silver nitrate although at least 80% of the bromine was removed from the compound. Further characterization was not attempted. However, the results do demonstrate that ring opening has occurred in preference to substitution in this case also.

The appearance of a dibromide as the main isolable product of reaction between an olefin and N-bromosuccinimide has been noted previously by several investigators. Olefins involved include

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[1] From the Master's theses of S. C. Caywood (1950), W. F. Boyce (1951) and F. L. Langevin, Jr., (1953).

[2] See for example H. Gilman, ed., "Organic Chemistry, an Advanced Treatise," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., 1943, p. 75 ff.; E. E. Royals, "Advanced Organic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1954, p. 210 ff.

[3] R. H. Eastman, This Journal, **76**, 4115 (1954).

[4] L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3840 (1951).

[5] H. C. Brown and M. Gerstein, *ibid.*, **72**, 2926 (1950); H. C. Brown, R. S. Fletcher and R. B. Johannsen, *ibid.*, **73**, 212 (1951).

[6] H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

[7] G. S. Hammond and R. W. Todd, *ibid.*, **76**, 4081 (1954).

[8] J. D. Roberts and P. H. Dirstine, *ibid.*, **67**, 1281 (1945).

[9] M. S. Kharasch, M. Z. Fineman and F. R. Mayo, *ibid.*, **61**, 2139 (1939).

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

[11] See C. Djerassi, *Chem. Revs.*, **43**, 271 (1948).

[12] E. P. Kohler and J. B. Conant, This Journal, **39**, 1404 (1917).

methylenecyclobutane,[13a] cyclobutene,[13b] ethyl tetrolate,[14] benzalacetone[15] and ethyl vinylacetate.[16] The course of the reaction can be changed from predominating substitution to predominating addition by the addition of a trialkylammonium halide.[17]

Experimental

1-Phenyl-2-alkylcyclopropanes.—These were prepared by the method used by Davidson and Feldman[18] and had the same physical constants. A Prileschaev olefin determination with peroxyacetic acid on the ethyl analog showed the presence of 4 mole % of unsaturation.

Bromination of 1-Phenyl-2-isopropylcyclopropane.—In a typical experiment 30 g. (0.19 mole) of 1-phenyl-2-isopropylcyclopropane, 70 g. (0.39 mole) of N-bromosuccinimide and 3.0 g. (0.02 mole) of benzoyl peroxide were added to 80 ml. of carbon tetrachloride in 250-ml. round-bottom flask fitted with a condenser. The mixture was refluxed for four hours whence all of the N-bromosuccinimide was gone as shown by a starch–iodide test on the precipitate in the flask. The product was filtered and the carbon tetrachloride was removed under reduced pressure at room temperature. There was obtained 73 g. of a reddish oil. No appreciable reaction in 24 hr. was noted if the benzoyl peroxide was omitted, whether heat was provided by a heating mantle or a General Electric drying lamp (250 watt).

When vacuum distillation of the oil was attempted, decomposition began at about 50° so purification was done by chromatographic adsorption. A column 38 mm. in diameter was packed to a depth of 70 cm. with Merck 200-mesh alumina. A solution of 13.3 g. of the oil in 100 ml. of 1:2 benzene–acetone was placed on the column and eluted with 1:3 benzene–ligroin. The fourth and fifth 100-ml. fractions of the percolate contained 6.3 g. of a light yellow oil. A dark band which remained near the top of the column was removed with ethanol and contained 5.2 g. of a dark intractable oil which was discarded. The results did not differ markedly if as little as 3 g. or as much as 20 g. of the oil was used. The average yield of the light yellow dibromide was 57%.

Anal. Calcd. for $C_{12}H_{16}Br_2$: mol. wt., 320; C, 45.04; H, 5.05; Br, 49.99. Found: mol. wt. (Rast), 307; C, 45.21; H, 5.08; Br, 49.71.

Dehydrobromination of the Dibromide.—To a solution of 32.5 g. (0.10 mole) of the dibromide in 500 ml. of 95% ethanol was added 22.5 g. (0.13 mole) of silver nitrate dissolved in the minimum amount of water. After 24 hr. the silver bromide was filtered off and the alcohol was distilled off under reduced pressure at 25–40° leaving 15.2 g. of an oil which absorbed bromine rapidly. Chromatographic adsorption on alumina as described above for the dibromide using benzene as the eluent yielded 12.9 g. (74%) of a light yellow oil. When 5.3 g. of this oil was fractionated through a Podbielniak type column there was obtained 3.2 g. of 1-phenyl-4-methyl-1,3-pentadiene-1,3, b.p. 124.5–126.5° (11 mm.), $n^{20}D$ 1.5977 (lit. 1.5985).[19]

Anal. Calcd. for $C_{12}H_{14}$: C, 91.09; H, 8.93. Found: C, 91.18; H, 8,92.

1-Phenyl-4-methylpentadiene-1,3 was prepared in 65% yield by dehydration of styrylisopropylcarbinol with potassium bisulfate at 145°. This preparation had b.p. 140–141° (20 mm.), $n^{20°}D$ 1.5983. The two samples of diene had identical ultraviolet absorption spectra showing a broad band $\lambda_{max.}$ 290 mμ, log ϵ 4.41, in 95% ethanol.

Tetrabromides were made from the two samples of diene using the procedure of Cheronis and Entrikin[20]: the tetrabromide from the dehydration product of the carbinol gave m.p. 142–143.5°; that from the dehydrobromination product of the dibromide m.p. 141–142°; a mixture m.p. 142–142.5°. The tetrabromide from the dehydrobromination product was analyzed.

Anal. Calcd. for $C_{12}H_{14}Br_4$: C, 30.15; H, 2.95; Br, 67.49. Found: C, 29.00; H, 2.92; Br, 67.36.

Bromination of 1-Phenyl-2-ethylcyclopropane.—The procedure was the same as that used for the isopropyl analog. However, the reaction was slower, 11 hr. being required for the complete consumption of the N-bromosuccinimide. The dibromide could be purified by chromatographic adsorption giving product with $n^{25}D$ 1.5721 or by distillation, b.p. 97–98° (0.45 mm.), $n^{25}D$ 1.5736, 23% yield.

Anal. Calcd. for $C_{11}H_{14}Br_2$: C, 43.17; H, 4.61; Br, 52.22; MR_D, 64.95. Found: C, 43.34; H, 4.72; Br, 52.21; MR_D, 65.13; d^{25} 1.5464.

Reaction of 12.0 g. (0.0825 mole) of 1-phenyl-2-ethylcyclopropane with 13.2 g. (0.0825 mole) of bromine in 70 ml. of carbon tetrachloride yielded 18.4 g. (72.8%) of dibromide, b.p. 106–109° (0.7 mm.), $n^{25}D$ 1.5724; Br, 52.97. The infrared spectra of the two dibromides were identical.

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[13] (a) E. R. Buchman and D. R. Howton, THIS JOURNAL, **70**, 2517 (1948); (b) **70**, 3510 (1948).

[14] J. English, Jr., and J. D. Gregory, *ibid.*, **71**, 1115 (1949).

[15] P. L. Southwick, L. A. Pursglove and P. Numerof, *ibid.*, **72**, 1600 (1950).

[16] E. J. Corey, *ibid.*, **75**, 2251 (1953).

[17] E. A. Braude and E. S. Waight, *J. Chem. Soc.*, 1116 (1952).

[18] D. Davidson and J. Feldman, THIS JOURNAL, **66**, 489 (1944).

[19] W. S. Emerson, *J. Org. Chem.*, **10**, 466 (1945).

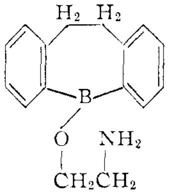
[20] N. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Crowell Co., New York, N. Y., 1947, p. 315.

Organoboron Compounds. VI.[1] Preparation of a Heterocyclic Organoboron Compound

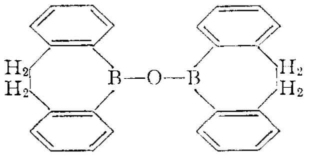
BY ROBERT L. LETSINGER AND IVAN H. SKOOG

RECEIVED MARCH 9, 1955

The techniques which were developed for the preparation of aminoethyl diphenylborinate[2] were used to synthesize 5-β-aminoethoxy-10,11-dihydrodibenzo[b,f]borepin (I). To our knowledge, this is the first example of the isolation of a heterocyclic compound which has only carbon and boron in the ring.



I



II

o,o'-Dilithiobibenzyl, prepared by a metal halogen interchange between butyllithium and dibromobibenzyl, was allowed to react with butyl borate in ether solution at about −70°. After hydrolysis, the products of the reaction were esterified with butyl alcohol and distilled. Compound I was obtained in 42% yield from the reaction of the impure butyl ester with ethanolamine. On hydrolysis and drying, compound I was converted to the oxide II in 96% yield.

The structure for I is based on the method of synthesis, analytical data, and the fact that bromine and hydrogen peroxide reacted with I to give good yields of *o,o'*-dibromobibenzyl and *o,o'*-dihydroxybibenzyl, respectively. Furthermore, bibenzyl was formed when the oxide II was heated with aqueous zinc chloride and with palladium-on-charcoal.

Experimental Part

o-**Bromobenzyl Bromide.**—Bromine (172 ml., 3.35 moles) was added dropwise over a three-hour period to 547 g. (3.35

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[1] For the previous paper in this series see R. L. Letsinger and N. Remes, THIS JOURNAL, **77**, 2489 (1955).

[2] R. L. Letsinger and I. H. Skoog, *ibid.*, **77**, 2491 (1955).