[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ILLINOIS INSTITUTE OF TECHNOLOGY]

Halogenation of Olefins in Heterocyclic Tertiary Amines. I. Cycloalkenes[1]

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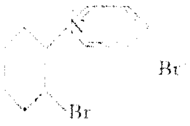
Many studies have been reported on the halogenation of olefins in the presence of various anions and neutral molecules which successfully enter into the reaction.[3,4]

In this manner, Francis[5] isolated 2-chloroethyl bromide from the bromination of ethylene in the presence of sodium chloride and Weber, Hennion and Vogt[6] found 2-chloroethyl acetate in the products of the chlorination of ethylene in acetic anhydride.

Barnett, Cook and Peck[7] obtained a quaternary salt, along with 1,2-dibromocyclohexane, from the bromination of cyclohexene in pyridine. The structure of the salt was not established, but it was thought to be 1-(2-bromocyclohexyl)-pyridinium bromide (I).



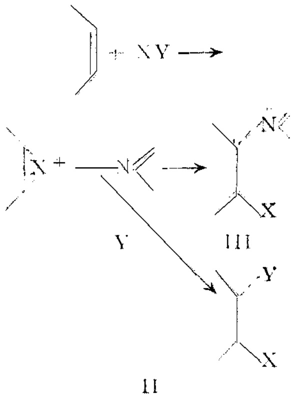
I

In this study, the reaction has been explored with cyclohexene and cyclopentene by using bromine and iodine monochloride as halogens and pyridine, quinoline and isoquinoline as bases. The quaternary salts which were isolated are itemized in Table I.

An elucidation of the structure of these salts was effected by hydrogenation of I to the corresponding piperidinium salt which was hydrolyzed to the known 1-(*trans*-2-hydroxycyclohexyl)-piperidine.[8] The over-all yield from I was 70%. This hydrolysis is considered to proceed through a cyclohexene iminium ion and give over-all retention of configuration.[9]

The compounds related to I are therefore designated as *trans*-2-halocycloalkyl quaternary salts. The products of the iodine monochloride reactions are *trans*-2-iodocycloalkyl quaternary chlorides because of their rapid production of silver chloride when treated with silver nitrate.

An insight into the reaction mechanism was obtained from the observations that the yield of increased with the ratio of pyridine to cyclohexene and that decreasing yields of the corresponding quaternary salts resulted from replacing pyridine with isoquinoline and quinoline. Considering, in addition, the doubled yield of quaternary salt when iodine monochloride was substituted for bromine in the reaction involving cyclohexene and pyridine, it is concluded that a competition may be operating between the halide ion and the base in the halogenation mechanism,[10-13] as shown in the following representation.



That III is not formed directly from II and the base is shown by the recovery in good yield of 1,2-dibromocyclohexane and 1-iodo-2-chlorocyclohexane after reactions with pyridine[14] under the conditions of the halogenation reactions.

Experimental[15]

Starting Materials.—Cyclohexene (b. p. 83°) and pyridine (b. p. 114–115°) were redistilled Paragon products. Quinoline (b. p. 107° *ca.* 11 mm.) and isoquinoline (b. p. 104°, 8 mm.) were redistilled Reilly products. Cyclopentene (b. p. 45–46°) was obtained from Columbia Organic Chemicals Co., Inc. Iodine monochloride (b. p. 97°) was a redistilled Eastman Kodak Co. product.

Halogenation Procedure.—Table I gives the numerical data for the reactions, all of which were run in the following manner. To an ice-cooled solution of the olefin in the heterocyclic base, an equivalent quantity of bromine or iodine monochloride, with respect to the olefin, was added dropwise with efficient stirring. After a period of three hours, the insoluble material was separated and combined with any further material obtained from the filtrate by treatment with anhydrous ether. Recrystallization from hot acetone, containing just enough methanol to effect solution, gave the pure crystalline product. One reaction of cyclohexene and pyridine with iodine mono-

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(1) Presented before the Organic Division of the American Chemical Society, Atlantic City, September, 1949.

(2) Vitamins, Inc., Chicago, Illinois.

(3) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 148–151.

(4) Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, 2nd ed., pp. 43–45.

(5) Francis, THIS JOURNAL, **47**, 2340 (1925).

(6) Weber, Hennion and Vogt, *ibid.*, **61**, 1457 (1939).

(7) Barnett, Cook and Peck, *J. Chem. Soc.*, **125**, 1035 (1924).

(8) Kusner, *Ukrain. Khem. Zhur.*, **7**, Wiss. Abt. 179–183 (1932).

(9) Winstein and Grunwald, THIS JOURNAL, **70**, 834 (1948).

(10) Bartlett and Tarbell, *ibid.*, **58**, 466 (1936).

(11) Roberts and Kimball, *ibid.*, **59**, 947 (1937).

(12) Nozaki and Ogg, *ibid.*, **64**, 715 (1942).

(13) Winstein, *ibid.*, **64**, 2793 (1942).

(14) 1,2-Dibromocyclohexane reacts with quinoline at 185–190° to give benzene, cyclohexadiene, cyclohexene and 1-bromocyclohexene; Willstätter and Hatt, *Ber.*, **45**, 1467 (1912).

(15) Carbon, hydrogen and nitrogen analyses by Micro-Tech Laboratories, Skokie, Illinois, and bromide analyses by Harold E. Zenisek. Melting points taken on a Fisher–Johns block

TABLE I

trans-2-HALOCYCLOALKYL QUATERNARY SALTS

				Analytical data, %							
				Bromide		Carbon		Hydrogen		Nitrogen	
Name	Yield,[a] %	M. p., °C.	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1-(2-Bromocyclohexyl)-pyridinium bromide	30[b]	170–172	$C_{11}H_{15}NBr_2$	24.89	24.32						
2-(2-Bromocyclohexyl)-isoquinolinium bromide	14	203–205	$C_{15}H_{17}NBr_2$	21.54	21.32						
1-(2-Bromocyclohexyl)-quinolinium bromide	3.5	165–167	$C_{15}H_{17}NBr_2$	21.54	21.37						
1-(2-Iodocyclohexyl)-pyridinium chloride	67	154–156 (dec.)	$C_{11}H_{15}NClI$			38.67[c]	38.93	5.02[c]	5.01	4.10[c]	4.05
1-(2-Iodocyclohexyl)-pyridinium chloroiodate (I)	[d]	119–120	$C_{11}H_{15}NCl_2I_2$			26.21[c]	26.17	3.39[c]	3.04	2.78[c]	2.77
1-(2-Iodocyclopentyl)-pyridinium chloride	34	107–108	$C_{10}H_{13}NClI$			36.66[c]	36.90	4.62[c]	4.61	4.27[c]	4.21
1-(2-Bromocyclopentyl)-pyridinium bromide	17	108–110	$C_{10}H_{13}NBr_2$	26.03	26.00						

[a] Ratio, olefin to base, 1:4. [b] 41% at 1:12; 17% at 1:1. [c] Analysis was calculated for the monohydrate. [d] Described in the last paragraph of "halogenation procedure" in the experimental.

chloride was run with an addition time of fifty minutes and then immediately treated with ether to give a solid product which was extracted with acetone to give a white crystalline material and a red filtrate. The former was identical with the product from the normal three-hour reaction. Anhydrous ether was quickly added to the filtrate, throwing out 1-(*trans*-2-iodocyclohexyl)-pyridinium chloroiodate (I) in 14.5% yield as an orange solid crystallizing in rosettes. Prolonged treatment of this compound with acetone produced 80% of 1-(*trans*-2-iodocyclohexyl)-pyridinium chloride.

1,2-Dibromocyclohexane.—The ethereal filtrate from the reaction of cyclohexene and quinoline with bromine was washed well with cold dilute hydrochloric acid and then with water. After drying over anhydrous sodium sulfate, the ether was removed at atmospheric pressure and the residue fractionated under reduced pressure, giving a 74% yield of 1,2-dibromocyclohexane, b. p. 90° (9.5 mm.),[16] $n^{32}D$ 1.5490.

Reactions of Pyridine with 1,2-Dibromocyclohexane and with 1-Iodo-2-chlorocyclohexane.—A mixture of 29.8 g. (0.123 mole) of 1,2-dibromocyclohexane and 39.7 g. (0.493 mole) of pyridine was kept at 0° for three hours, at the end of which time, addition of anhydrous ether gave no insoluble material. The ether solution was washed free of pyridine with acid, dried and then distilled, giving 28.1 g. (94.4%) of 1,2-dibromocyclohexane, b. p. 87.5° (9 mm.). A similar reaction with 1-iodo-2-chlorocyclohexane[17] gave a 67% recovery of the dihalide, b. p. 115–117° (14 mm.), $n^{26}D$ 1.5685.

Hydrogenation of 1-(*trans*-2-Bromocyclohexyl)-pyridinium Bromide.—A solution of 30.9 g. of 1-(*trans*-2-bromocyclohexyl)-pyridinium bromide in 50 ml. of methanol containing 0.1 g. platinum oxide catalyst was hydrogenated at room temperature and at an initial pressure of three atmospheres. After three hours, the pressure became constant at a value corresponding to a hydrogenation of three double bonds per molecule. The catalyst was filtered off and anhydrous ether added to the filtrate throwing out 27.1 g. (86%) of a white crystalline solid. *Anal.* Calcd. for $C_{11}H_{21}NBr_2$: C, 40.39; H, 6.47; N, 4.28; Br^-, 24.43. Found: C, 40.64; H, 6.40; N, 4.07; Br^-, 24.65, 24.38. This material had no characteristic melting point.

Hydrolysis of 1-(*trans*-2-Bromocyclohexyl)-piperidinium Bromide.—A solution of 32.7 g. of 1-(*trans*-2-bromocyclohexyl)-piperidinium bromide in 100 ml. of water was refluxed with 11.2 g. of potassium hydroxide for one hour. On cooling the reaction mixture, the upper layer crystallized. It was filtered in the cold, washed with ice-water, and dried in a vacuum desiccator over potassium hydroxide. There was obtained 14.6 g. (80%) of 1-(*trans*-2-hydroxycyclohexyl)-piperidine,[8] m. p. 34.5–35°, b. p. 94–96° (1 mm.). *Anal.* Calcd. for $C_{11}H_{21}ON$: C, 72.08; H, 11.55; N, 7.64. Found: C, 72.38; H, 11.65; N, 7.51.

Summary

1. A study has been made of the halogenation of cycloalkenes in the presence of heterocyclic tertiary amines. *trans*-2-Halocycloalkyl quaternary salts have been obtained from reactions involving cyclohexene, cyclopentene, pyridine, isoquinoline and quinoline with bromine and iodine monochloride.

2. In the bromination, the yield of quaternary salt increased with the ratio of base to olefin and followed the series: pyridine > isoquinoline > quinoline.

3. The yields from the iodine monochloride reactions were much higher than from the corresponding brominations.

4. 1,2-Dibromocyclohexane and 1-iodo-2-chlorocyclohexane were unreactive to pyridine at 0°.

5. A mechanism has been proposed involving competition of base and halide anion for a halonium ion intermediate.

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[16] Snyder and Brooks, "Organic Syntheses," Coll. Vol. II, 1943, p. 172.

[17] Brunel, *Ann. chim.*, [8] **6**, 284 (1905).