Catalysis by Certain Amines in an Aqueous Phase. Preparation of Dichlorocyclopropane Derivatives

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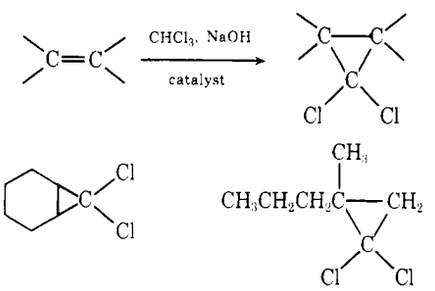
Received April 25, 1974

Dihalocarbenes are considered synthetically useful species for cyclopropane ring formation. The preparation of dichlorocyclopropane derivatives with concentrated aqueous sodium hydroxide and chloroform in the presence of quaternary ammonium or phosphonium salts was recently reported.[1-3] On the other hand, it is said that tertiary amines have catalytic effect for some reactions between aqueous and organic layers.[4,5]

We now report the catalytic effect of tertiary amines for the preparation of dichlorocyclopropane derivatives by the reaction of olefins with concentrated aqueous sodium hydroxide and chloroform.

The reaction was carried out using cyclohexene or 2-methyl-1-pentene with tertiary amines as the catalyst to give dichloronorcarane (**1**) and 1-methyl-1-*n*-propyl-2,2-dichlorocyclopropane (**2**), respectively. As tertiary amines,



trialkylamines (C_2–C_6, C_8, and C_{10}), *N*-*n*-butylpiperidine, *N*,*N*-diethylaniline, and triethanolamine were used. Primary amines, secondary amines, tertiary amine hydrogen halides, and tetraalkylammonium halides were used, in order to study the catalytic effect of other amines or quaternary ammonium salts. The results of catalytic effects of some amines and ammonium salts in the formation of dichloronorcarane are given in Table I.

We found that trialkylamines, their hydrogen halides, and the corresponding tetraalkylammonium halides showed significant catalytic effects, but the primary and secondary amines did not. Trialkylamines exhibited the same effects as trialkylamine hydrogen halides and tetraalkylammonium halides. For example, tri-*n*-butylamine gave **1** in 75% yield, and in the cases of tri-*n*-butylamine hydrogen chloride and tetra-*n*-butylammonium bromide, the yields of **1** were 77 and 76%, respectively. In addition, trialkylamines having the alkyl groups of C_4 and C_5 showed better effects than other trialkylamines.

The catalytic effects of tertiary amines in the formation of **2** by the addition of a dichlorocarbene to 2-methyl-1-pentene were similar to those observed in the formation of **1**. The amines or ammonium salts (yield of **2**) follow: *N*-*n*-butylpiperidine (83%), *N*-*n*-butylpiperidine hydrogen bromide (86%), *N*,*N*-di-*n*-butylpiperidinium iodide (86%).

Thus, we found that trialkylamine was able to form a dichlorocarbene from chloroform and to give dichlorocyclopropane derivatives. An experiment using stoichiometric quantities of olefin (44 mmol) and trialkylamine (44 mmol) in chloroform (11 ml, 135 mmol) without aqueous sodium hydroxide at 50° for 2 hr failed to form dichlorocyclopropane derivatives. Therefore, it seems likely that trialkylamine does not react directly with chloroform; the sodium hydroxide appears to be essential for the formation of dichlorocarbene.

It is very interesting that trialkylamine is effective in this phase transfer catalysis reaction.

Experimental Section

Melting points are uncorrected. Mass spectra were run on a Hitachi RMU-6E mass spectrometer. Infrared spectra were recorded on a Hitachi Model 215 infrared spectrophotometer. Gas chromatographic analyses were performed on a Hitachi Model 063 gas chromatograph using a 3 mm × 1 m column of Silicone SE-30 on

Table I
Catalytic Effects of Amines and Quaternary Ammonium Salts in the Formation of Dichloronorcarane

Amine or quaternary ammonium salt	Yield of dichloronorcarane, %	Amine or quaternary ammonium salt	Yield of dichloronorcarane, %
None	<1	Tri-*n*-decylamine	45
Triethylamine	33	*n*-Laurylamine	<1
Triethylamine hydrogen chloride	35	Piperidine	<1
		N-*n*-Butylpiperidine	73
Tetraethylammonium chloride	31	*N*-*n*-Butylpiperidine hydrogen bromide	76
Tri-*n*-propylamine	67	*N*,*N*-Di-*n*-butylpiperidinium iodide	75
n-Butylamine	<1		
tert-Butylamine	4	Piperazine	<1
Di-*n*-butylamine	<1	Pyridine	<1
Tri-*n*-butylamine	75	*N*-*n*-Butylpyridinium bromide	<1
Tri-*n*-butylamine hydrogen chloride	77		
		N-*n*-Hexadecylpyridinium bromide	<1
Tetra-*n*-butylammonium bromide	76		
Tri-*n*-amylamine	73	Aniline	<1
Triisoamylamine	79	*N*-Ethylaniline	<1
Tri-*n*-hexylamine	65	*N*,*N*-Diethylaniline	<1
Tri-*n*-octylamine	65	Triethanolamine	<1

Chromosorb W AW (80–100 mesh). Elemental analyses were done on a Hitachi Model 026 CHN analyzer.

Reagents. Cyclohexene, 2-methyl-1-pentene, amines, and quaternary ammonium salts, except for some compounds described below, were commercial reagents and purified by distillation or recrystallization. Chloroform was commercial reagent and distilled twice.

Tri-*n*-butylamine hydrogen chloride was prepared by treatment of tri-*n*-butylamine with dry hydrogen chloride.[6]

***N*-*n*-Butylpyridinium bromide** was prepared from pyridine and *n*-butyl bromide by the method reported earlier.[7]

***N*-*n*-Butylpiperidine** was prepared from piperidine and *n*-butyl bromide by the method reported earlier.[8]

***N*-*n*-Butylpiperidine Hydrogen Bromide.** A solution of 2.4 g (25 mmol) of piperidine and 3.4 g (25 mmol) of *n*-butyl bromide in 20 ml of ethanol was refluxed for 2 hr. The reaction mixture was cooled and ethanol was removed. Dry ether was added to the residue and the mixture was stirred. A white solid was precipitated. The solid was washed with dry ether several times. It was recrystallized from absolute ethanol–ether (9:1) as white needles, mp 220–222°.

Anal. Calcd for $C_9H_{20}NBr$: C, 48.66; H, 9.07; N, 6.30. Found: C, 48.88; H, 9.41; N, 6.37.

***N,N*-Di-*n*-butylpiperidinium Iodide.** A solution of 2.4 g (25 mmol) of piperidine and 9.2 g (50 mmol) of *n*-butyl iodide in 20 ml of ethanol was refluxed for 0.5 hr. The reaction mixture was cooled and ethanol was removed. Dry ether was added to the residue and the mixture was stirred. A light yellow solid was precipitated. The solid obtained was collected by filtration and washed several times with dry ether. It was recrystallized from absolute ethanol–*n*-hexane (9:1) as light yellow needles, mp 222–223°.

Anal. Calcd for $C_{13}H_{28}NI$: C, 48.00; H, 8.68; N, 4.31. Found: C, 48.37; H, 8.87; N, 3.90.

Preparation of Dichlorocyclopropane Derivatives. A mixture of olefin (44 mmol), chloroform (11 ml, 135 mmol), and amine or quaternary ammonium salt (0.44 mmol) was stirred at 50°. An aqueous solution prepared from 13.5 g of sodium hydroxide and 27 ml of water was added during 15 min. After 2 hr of stirring the mixture was acidified with 10% sulfuric acid and extracted five times with 30-ml portions of ether. The combined ether extract was dried over calcium chloride, allowed to stand overnight, and evaporated to an oily liquid. The liquid was distilled and identified by mass spectrography. The yield of the product was determined by gas chromatography.

Dichloronorcarane (1). This compound was obtained from cyclohexene: bp 79–81° (15 mm) [lit.[9] bp 79–80° (15 mm)]; mass spectrum *m/e* 164 (P), 166 (P + 2); the P:(P + 2) ratio of relative intensity was *ca.* 3:2 (2 Cl). This material had an infrared spectrum identical with that of authentic dichloronorcarane.[10]

1-Methyl-1-*n*-propyl-2,2-dichlorocyclopropane (2). This compound was obtained from 2-methyl-1-pentene: bp 163–165°; mass spectrum *m/e* 166 (P), 168 (P + 2); the P:(P + 2) ratio of relative intensity was *ca.* 3:2 (2 Cl).

Acknowledgment. We thank Dr. S. Nakanishi for helping to obtain the mass spectra.

Registry No.—**1,** 823-69-8; **2,** 52259-98-0; chloroform, 67-66-3; cyclohexene, 110-83-8; 2-methyl-1-pentene, 763-29-1; tri-*n*-propylamine, 102-69-2; tri-*n*-butylamine, 102-82-9; tri-*n*-butylamine hydrogen chloride, 6309-30-4; tetra-*n*-butylammonium bromide, 1643-19-2; tri-*n*-amylamine, 621-77-2; triisoamylamine, 645-41-0; tri-*n*-hexylamine, 102-86-3; tri-*n*-octylamine, 1116-76-3; *N*-*n*-butylpiperidine, 4945-48-6; *N*-*n*-butylpiperidine hydrogen bromide, 51359-83-2; *N,N*-di-*n*-butylpiperidinium iodide, 52259-97-9.

References and Notes

(1) M. Makosza and M. Wawrzyniewicz, *Tetrahedron Lett.*, 4659 (1969).
(2) G. C. Joshi, N. Singh, and L. M. Pande, *Tetrahedron Lett.*, 1461 (1972).
(3) C. M. Starks, *J. Amer. Chem. Soc.*, **93,** 195 (1971).
(4) M. J. Jarrousse, *C. R. Acad. Sci., Ser. C,* **232,** 1424 (1951).
(5) Y. Yamamoto and T. Shimamura, *Kogyo Kagaku Zasshi,* **60,** 423 (1957).
(6) V. Deitz and R. M. Fuoss, *J. Amer. Chem. Soc.*, **60,** 2394 (1938). The pure sample was not obtained, because recrystallization of this compound was very difficult. In the earlier report, the purification of the compound was unsuccessful.
(7) M. Katcka and T. Urbanski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **12,** 615 (1964); *Chem. Abstr.*, **62,** 11662 (1965).
(8) H. W. Magnusson and E. R. Shierz, *Univ. Wyo., Publ.*, **7,** 1 (1940); *Chem. Abstr.*, **34,** 6867 (1940).
(9) W. I. Bevan, R. N. Haszelcline, and J. C. Young, *Chem. Ind. (London),* 789 (1961).
(10) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76,** 6162 (1954).