Reactions of Organic Anions; LXXVI[1].
A Convenient Procedure for the Generation of Bromochlorocarbene and Preparation of *gem*-Bromochlorocyclopropane Derivatives

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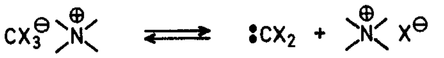
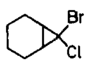
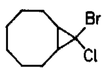
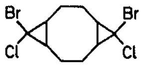
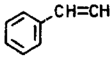
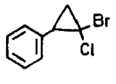
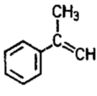
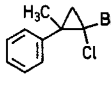
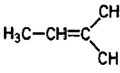
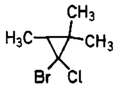
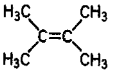
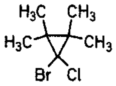
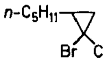
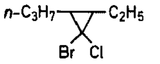
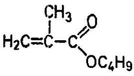
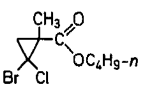
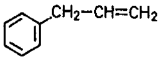
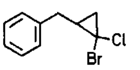
The presently most convenient modes of preparation of *gem*-dihalocyclopropanes are those using catalytic two-phase conditions in the generation of the dihalocarbenes[2], i.e., the action of concentrated aqueous sodium hydroxide on haloforms in the presence of alkenes and tetraalkylammonium salts. One of the characteristics of the system used is that the trihalomethyl anions (the precursors of the dihalocarbenes) entering the organic phase are accompanied by lypophilic tetraalkylammonium cations. Since the tetraalkylammonium salts with both trihalomethide and halide anions are well soluble in the organic phase, the formation of the dihalocarbenes is in fact a reversible process.



As a consequence, dihalocarbenes generated under catalytic two-phase conditions react more efficiently with alkenes than dihalocarbenes generated by other methods, e.g., from haloform and potassium *t*-butoxide. On the other hand, the equilibrium may impose limitations to the applicability of the catalytic two-phase method. Thus, Dehmlow has shown that treatment of chlorodibromomethane with aqueous sodium hydroxide and tetraalkylammonium salts results in the formation of all three possible dihalocarbenes, due to equilibration of the initially formed chlorodibromomethide anion[3]. Thus, catalytic two-phase conditions were regarded to be unsuitable for the synthesis of *gem*-bromochlorocyclopropanes from dihalocarbenes and alkenes. The present paper shows that this conclusion is not generally right.

Studying the influence of various catalysts on the properties and behaviour of dihalocarbenes I have found that the action of aqueous sodium hydroxide on chlorodibromomethane in the presence of dibenzo-18-crown-6 gives rise to bromochlorocarbene exclusively; with the alkenes present in the

Table. *gem*-Bromochlorocyclopropanes from Alkenes and Bromochlorocarbene generated under Catalytic Two-Phase Conditions

Alkene		Product	Yield[a] [%]	b.p. or m.p.	n_D^{20}	(Lit. n_D^{25})	Molecular formula[b]
	→		64	b.p. 77°/7 torr	1.5324	(1.5293)[4]	
	→		61	b.p. 129°/12 torr	1.5278	(1.5272)[5]	
	→		58[c]	m.p. 171–173.5°			$C_{10}H_{12}Br_2Cl_2$ (362.9)
	→		72	b.p. 104°/9 torr	1.5753	(1.5746)[5]	
	→		76	b.p. 115–116°/8 torr	1.5650		$C_{10}H_{10}BrCl$ (245.5)
 $H_3C{-}CH{=}C(CH_3)_2$	→		43	b.p. 47°/11 torr	1.4887		$C_6H_{10}BrCl$ (197.5)
 $(H_3C)_2C{=}C(CH_3)_2$	→		48	m.p. 63–65° (m.p. 63.5–65°)[5]			
$n\text{-}C_5H_{11}{-}CH{=}CH_2$	→		60	b.p. 82–83°/8 torr	1.4762	(1.4740)[5]	
$n\text{-}C_3H_7{-}CH{=}CH{-}C_2H_5$[d]	→		44	b.p. 77–78°/11 torr	1.4776		$C_8H_{14}BrCl$ (225.5)
 $H_2C{=}C(CH_3){-}C(O)OC_4H_9\text{-}n$	→		46	b.p. 124°/13 torr	1.4800		$C_9H_{14}BrClO_2$ (269.5)
	→		62	b.p. 140°/13 torr	1.5608		$C_{10}H_{10}BrCl$ (245.5)

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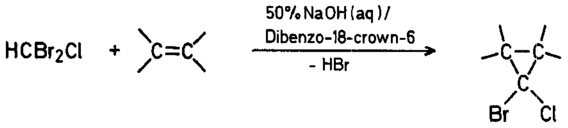
[a] Yield of isolated pure product. The purity was checked by G.L.C. (conditions: Chromatoprep N-502 instrument, 1 m column, 5% silicone oil OV-17 on Kieselguhr silanized with chlorotrimethylsilane.). The ^{1}H-N.M.R. spectra of all products were agreement with the expected structure.

[b] All new compounds gave satisfactory microanalyses: C, ±0.25; H, ±0.23.

[c] 0.01 mol of the diene was used.

[d] *cis/trans* mixture.

reaction mixture, the corresponding *gem*-bromochlorocyclopropanes are formed in high yields.



The results obtained depend strongly on the purity of the chlorodibromomethane used; contamination by other haloforms causes formation of substantial amounts of dichloro- and dibromocyclopropanes. It is also worth to point out, that dibenzo-18-crown-6 has the unique ability to cause a highly selective reaction. When other crown ethers (18-crown-6, 15-crown-5) were used as catalysts mixtures of three possible dihalocyclopropanes were obtained, although the selectivity was usually higher as compared to reactions catalyzed by tetraalkylammonium salts.

Chlorodibromomethane and bromodichloromethane can be prepared in high yield by reaction of a mixture of chloroform and bromoform with 50% aqueous sodium hydroxide in the presence of benzyltriethylammonium chloride[1].

Preparation of *gem*-Bromochlorocyclopropanes; General Procedure:

A mixture of the alkene (0.02 mol), chlorodibromomethane (4.2 g, 0.02 mol), 50% aqueous sodium hydroxide (6 ml), and dibenzo-18-crown-6 (0.15 g, ~0.4 mmol) is vigorously stirred at 45° for 4 h. The mixture is then diluted with water and extracted with dichloromethane. The extract is washed with water and dried with magnesium sulfate. The solvent is evaporated and the product purified by distillation under reduced pressure or by recrystallization.

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