A Simple Synthesis of *gem*-Bromochlorocyclopropanes via Phase-Transfer Catalysis[1]

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Substituted 1-bromo-1-chlorocyclopropanes **2** were synthesized from dibromomethane, phenyltrichloromethane trichloride and alkenes **1** in the presence of 60 % aqueous potassium hydroxide and tetrabutylammonium hydrogen sulfate as a catalyst (PTC system), in good yields.

gem-Dichloro- or dibromocyclopropanes are easily available from the corresponding haloforms (HCX_3, X = Cl, Br) and alkenes in the presence of concentrated aqueous alkali metal hydroxides and a quaternary ammonium salt as a catalyst.[2] On the other hand, pure *gem*-bromochlorocyclopropanes cannot be synthesized from dibromochloromethane and alkenes under the same conditions, with typical PTC catalysts, since they are notoriously contaminated with both *gem*-dichloro-, and *gem*-dibromoderivatives.[3] However, pure title products are easily prepared if the phase-transfer catalyzed reaction with dibromochloromethane is carried out with dibenzo-18-crown-6,[4] some other crown ethers or tetramethylammonium chloride[5] as the catalyst.

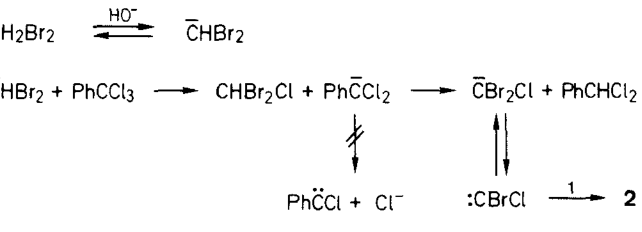
Searching for new methods for the synthesis of *gem*-dihalocyclopanes we have found that dichloromethane or dibromomethane, carbon tetrachloride and alkenes, afforded in the PTC system *gem*-dichlorocyclopropanes.[6]

We now wish to report that simple stirring of dibromomethane, phenyltrichloromethane and alkenes **1** with an excess of 60 % aqueous potassium hydroxide and tetrabutylammonium hydrogen sulfate (TBAHS) as a catalyst, at ambient temperature, resulted in the formation of *gem*-bromochlorocyclopropanes **2** in good yield (Table).

Scheme 1

Phenyldichloromethane was the second product formed, in yields corresponding to those of **2**. The yield of **2** decreased when an excess of phenyltrichloromethane was used (eg. **2b**, to 50 %). Alkenes **1** of different reactivity can be applied in this preparation of **2**. Only with alkenes **1** of relatively low nucleophilicity (eg. **2f**), a small amount of the corresponding *gem*-dibromocyclopropane was formed. When the boiling points of product **2**, phenyltrichloromethane and phenyldichloromethane are similar, the isolation of **2** by distillation is difficult (e.g. **2c–e**).

Mechanistically, this process consists of deprotonation of dibromomethane, chlorination of dibromomethyl carbanion by means of phenyltrichloromethane, and fast protonation of the resultant phenyldichloro carbanion, which apparently does not dissociate rapidly into chlorophenylcarbene and chloride ion. Since the latter anion is not present in the system, contrary to the case when carbon tetrachloride is used instead of phenyltrichloromethane,[6] bromochlorocarbene formed from dibromochloro carbanion reacts with **1** to give **2** (Scheme **2**).



Scheme 2

To summarize, our method for the preparation of **2** starts from easily available and inexpensive substrates, and may be considered as competitive for existing ones.[4,5]

Table. *gem*-Bromochlorocyclopropanes **2** Prepared

1,2	R[1]	R[2]	R[3]	R[4]	Reaction Temp. (°C)	Yield of **2** (%)	**2**,[a] bp (°C)/Torr or mp (°C)	
							found	Lit.[4]
a	Me	Me	Me	Me	25	60	63–65 (MeOH)	63–65
b	Me	Me	Me	H	25	75	50/12	47/11
c	Ph	H	Me	H	45	71[b]	[c]	115–116/8
d	$-(CH_2)_6-$		H	H	45	70[b]	[c]	129/12
e	$-(CH_2)_2CH{=}CH(CH_2)_2-$		H	H	45	55[b,d]	[c]	–
f	MeO	H	Me	H	25	50	55/37	–
g	Bn	H	H	H	45	47[e]	138–142/20	140/13

[a] The products **2** were compared with authentic samples.[4]
[b] Calculated from GC.
[c] See General Procedure.
[d] Bis-adduct was isolated with yield 9%.
[e] This product contains *gem*-dibromo derivative, yield ca. 3%.

GC analyses were carried out on a Chromatron GCHF 18,3 instrument with a FID detector, using OV 17 column (silicon oil OV 17, 3% on Chromosorb W). In all cases (except of **1g**, see Table), only the peaks of **2**, $PhCHCl_2$ and $PhCCl_3$, all well resolved, were observed. Independently synthesized[2] adducts of dichlorocarbene to **1c,d** exhibited peaks which did not overlap with the peaks of the components of the corresponding crude mixtures. Amount of *gem*-dichloro- and/or dibromocyclopropanes is evaluated to be $\leq 1.0\%$. Microanalyses were obtained using a Perkin-Elmer 240 C, H, N. analyser. ^{1}H-NMR spectra were recorded on a Varian VXR-300 spectrometer.

Commercially available alkenes **1**, CH_2Br_2 and $PhCCl_3$ were purified by distillation. TBAHS (Bofors, Nobel Kemi) was used without further purification. Authentic samples of **2** were prepared according to literature procedures.[4] From **1e** (5.4 g, 50 mmol), $CHBr_2Cl$ (15.6 g, 75 mmol), 50% aq NaOH (8 mL) and 18-crown-6 (0.1 g, 0.27 mmol), **2e** [yield: 4.2 g (36%)], bp 115–117°C/6 Torr and the bis-adduct [yield: 3.0 g (17%)] are obtained.

2e: $C_9H_{12}BrCl$ calc. C 45.89 H 5.13
(235.5) found 46.25 5.08

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 1.3–2.5$ [4 m, 10 H, $(CH_2)_2CH(C)CH(CH_2)_2$], 5.4–5.6 (m, 2 H, HC=CH).

1-Bromo-1-chlorocyclopropanes 2; General Procedure:

CH_2Br_2 (3.48 g, 20 mmol), alkene **1** (10 mmol), $PhCCl_3$ (1.95 g, 10 mmol; in the case of **1e**, 3.91 g, 20 mmol), TBAHS (0.2 g, 0.6 mmol), and 60% aq KOH (7 mL) are vigorously stirred at the temperature indicated in the Table, for 21 h. The mixture is diluted with H_2O (20 mL), extracted with CH_2Cl_2 (3 × 10 mL), the organic extracts are washed with H_2O (15 mL), dried ($MgSO_4$), and the solvent is evaporated. The products are isolated as described below

2a: the solid is filtered and crystallized.

2b,f,g: the products are fractionally distilled in vacuo.

2f: C_5H_8BrClO calc. C 30.11 H 4.04
(199.5) found 30.38 4.22

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 1.46$ (d, 1 H, J = 8.3 Hz, $CH_{cyclopropyl}$), 1.62 (s, 3 H, CH_3), 1.70 (d, 1 H, J = 8.3 Hz, $CH_{cyclopropyl}$), 3.45 (s, 3 H, CH_3O).

2c: the fraction of bp 132–136°C/25 Torr is collected, it consists of **2c**, $PhCCl_3$ and $PhCHCl_2$.

2d: the fraction of bp 134–137°C/20 Torr is collected, it consists of **2d**, $PhCCl_3$ and $PhCHCl_2$.

2e: the crude products are filtered to give bis-adduct mp 172–174°C, MeOH (Lit.[4] mp 171–173.5°C), yield: 0.33 g (9%), the filtrate is distilled, and the fraction of bp 118–121°C/12 Torr which consists of **2e**, $PhCCl_3$ and $PhCHCl_2$ is collected.

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(1) Reactions of Organic Anions, Part 184; Part 183, see: Mąkosza, M.; Kwast, E. *Tetrahedron*, in press.
(2) Dehmlow, E.V.; Dehmlow, S.S. *Phase Transfer Catalysis*, 2nd Ed., Verlag Chemie, Weinheim, 1983.
Mąkosza, M.; Fedoryński, M., in: *Advances in Catalysis*, Vol. 35, Academic Press, New York, 1987, p. 375.
(3) Dehmlow, E.V.; Lissel, M.; Heider, J. *Tetrahedron* **1977**, *33*, 363.
(4) Fedoryński, M. *Synthesis* **1977**, 783.
(5) Dehmlow, E.V.; Stütten, J. *Liebigs Ann. Chem.* **1989**, 187.
(6) Jończyk, A.; Balcerzak, P. *Tetrahedron Lett.* **1989**, *30*, 4797.