A flexible Route to 1-Bromo-2-alkylcyclopropenes

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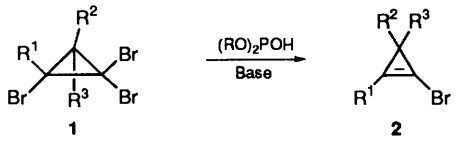
1,1,2-Tribromocyclopropanes undergo 1,2-debromination with a dialkyl phosphite and either a trialkylamine or sodium hydride to form the corresponding 1-bromocyclopropene.

1,1,2-Trihalogenocyclopropanes undergo efficient 1,2-dehalogenation with methyllithium to give a 1-halogenocyclopropene which, in some cases, reacts further with a second equivalent of methyllithium, to afford a 1-lithiocyclopropene.[1] A similar 1,2-dehalogenation of 1,2-diiodocyclopropanes is induced by sodium hydroxide,[2] butyllithium,[3] or zinc and ultrasound.[4] It is known that diethyl phosphite and triethylamine at elevated temperature efficiently reduces alkyl and aryl substituted 1,1-dibromocyclopropanes to 1-bromocyclopropanes and that 1,2-dibromostilbene undergoes competitive dehalogenation and dehydrohalogenation with this reagent;[5] we now report that similar treatment of a 1,1,2-tribromocyclopropane provides an efficient and very convenient route to a 1-bromocyclopropene.

Treatment of the tribromide **1** (R^1 = octyl, R^2 = R^3 = H) with diethyl phosphite and triethylamine at 20 °C for 1 h followed by work-up led to 1-bromo-2-octylcyclopropene **2** (R^1 = octyl, R^2 = R^3 = H) (95%), identical with an authentic sample.[1] The relatively low temperature at which this occurred is in line with the reduction of 1,1-dibromocyclopropanes by diethyl phosphite and triethylamine, which occurred at room temperature when an electron-withdrawing group was present on C-2.[5] Using this same method, the lower homologues **2**

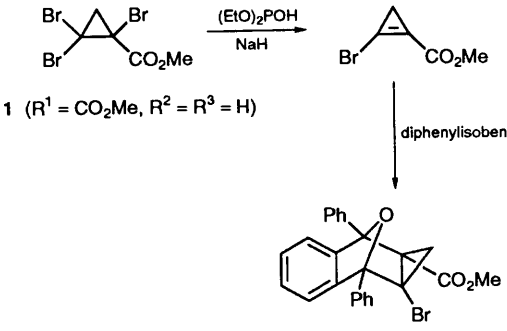


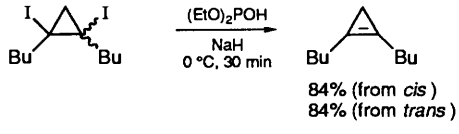
1 **2**

(R^1 = pentyl, butyl and ethyl, R^2 = R^3 = H) were obtained in good or moderate yield (see Table 1). The same cyclopropenes were obtained when the tribromocyclopropanes were treated either with dioctyl phosphite and triethylamine, or with either diethyl or dioctyl phosphite and sodium hydride; the use of dioctyl phosphite and either tripropylamine or tributylamine led to slower reactions at 20 °C, and the cyclopropene was accompanied by *cis*- and *trans*-1,2-dibromo-1-alkylcyclopropanes.

Although the yields decreased as the size of the alkyl group was reduced, it was possible with **1** (R^1 = Et or Me, R^2 = R^3 = H) to avoid any work up by treating them with dioctyl phosphite and sodium hydride *in vacuo* (1 mmHg) and continuously distilling the products into a cold trap.† It was also possible to carry out the eliminations in the presence of a diene such as diphenylisobenzofuran and to trap the derived cyclopropenes *in situ*. In this way, the tribromo ester **1** (R^1 = CO_2Me, R^2 = R^3 = H)[6] was debrominated and the resulting cyclopropene trapped in moderate yield (50%).

The isomeric *cis*- and *trans*-1,2-dibutyl-1,2-diiodocyclopropanes[3] both reacted rapidly with diethyl phosphite and sodium hydride at 0 °C to form 1,2-dibutylcyclopropene in 84% yield in each case. Similar eliminations from both isomers of 1,2-dibromo-1,2-dimethylcyclopropane using an alkyllithium have been reported[7] and both diiodides are also known to undergo elimination on reaction with butyllithium.[3] However, while the reaction of the *cis*-diiodide with diethyl phosphite and triethylamine was complete in 20 h, the *trans*-isomer remained largely unchanged under these conditions.





The reaction of tetrabromides with a dialkyl phosphite and base was rather more complex, apparently because the derived dibromocyclopropene could react further with the reagents. The reaction of **1** (R^1 = Br, R^2 = R^3 = H)‡ in the absence of a trapping agent gave only a very low yield of 1,2-dibromocyclopropene; however, when carried out in the presence of diphenylisobenzofuran, the [4 + 2] cycloadduct of the cyclopropene[8] was isolated (76%). Reaction of the dimethyl tetrabromide **1** (R^1 = Br, R^2 = R^3 = Me) with an excess of dioctyl phosphite and sodium hydride gave no trapping of the cyclopropene, but a similar reaction in the presence of 2,3-dimethylbut-2-ene trapped the allene **4** (R^2 = R^3 = Me) in moderate yield (39%). This may arise by 1,2-debromination of the cyclopropene to the allenic carbene **5**, and trapping of this by the alkene, or by ring-opening of the intermediate cyclopropene to a vinylcarbene **6**,[9] trapping of this by the alkene and debromination of the resultant bromo-1-(1-bromovinyl) cyclopropane by an excess of phosphite and sodium hydride.

Experimental

Sodium hydride (0.012 g, 0.51 mmol) was added to a stirred solution of 1,1,2-tribromo-2-octylcyclopropane (0.20 g, 0.511

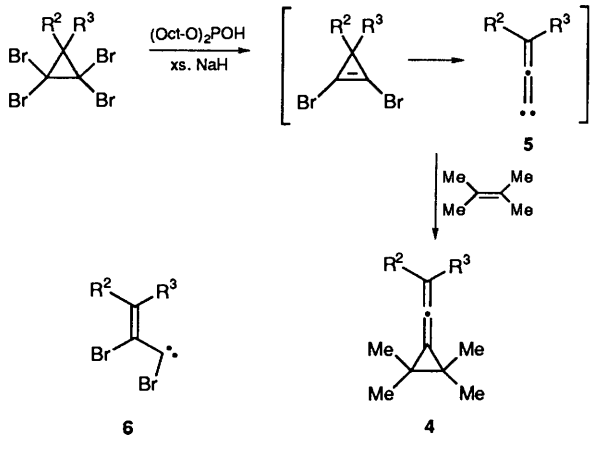
† Reaction of **1** (R^1 = Et, R^2 = R^3 = H) with either diethyl phosphite or dibutyl phosphite and tributylamine under these conditions did give the cyclopropene, but mixed with bromoethane and bromobutane, respectively, derived from the dialkyl phosphite. The structures of these products were confirmed by GLC, GC-MS and NMR.

‡ Thanks are due to J. R. Al Dulayymi and P. Tomasin for providing this compound.

Table 1 1,2-Debromination of 1,1,2-tribromocyclopropanes to cyclopropenes **2** by a dialkyl phosphite and base

Cyclopropane **1**					Conditions	
R^1	R^2	R^3	Phosphite	Base	T/°C (t/min or h)	Cyclopropene (%)
Oct	H	H	Diethyl	Et_3N	20 (20 min)	95‡
Oct	H	H	Diethyl	NaH*	0–20 (5 min)	96
Oct	H	H	Dioctyl	NaH*	0–20 (5 min)	96
Pen	H	H	Diethyl	Et_3N	20 (20 min)	93
Pen	H	H	Diethyl	NaH*	0–20 (5 min)	64
Pen	H	H	Dioctyl	NaH†	0–20 (5 min)	90
Pen	H	H	Dioctyl	Et_3N	20 (1 h)	73§
Bu	H	H	Diethyl	Et_3N	20 (1 h)	69
Et	H	H	Diethyl	Et_3N	20 (1 h)	63
Et	H	H	Dioctyl	NaH	20 (30 min)	52¶
Me	H	H	Diethyl, THF	NaH	0 (18 h)	80‖
Me	Me	H	Diethyl	NaH	0 (18 h)	69**
CO_2Me	H	H	Diethyl, THF	NaH	0 (18 h)	50††
Br	H	H	Diethyl	Et_3N	20 (18 h)	76‡‡
Br	Me	H	Diethyl, THF	NaH	0 (18 h)	36§§

* 1 mol. equiv. † NaH (6 mol. equiv.) and phosphite (8 mol. equiv.). ‡ Replacing the triethylamine with dimethylaminopyridine, tripropylamine and dibutylamine gave the same product in yields of 88, 84 and 84% after 4 h, 30 min, and 30 min, respectively, at 20 °C. Replacing it with tributylamine for 20 h or trioctylamine for 4 h gave a mixture of the cyclopropene with *trans*- and *cis*-1,2-dibromo-1-octylcyclopropanes. § Together with small amounts of *trans*- and *cis*-1,2-dibromo-1-pentylcyclopropanes. When this reaction was repeated using dioctyl phosphite and tripropylamine for 20 h at 20 °C, a mixture of the cyclopropene and dibromides was obtained in ratio *ca.* 2:1. ¶ Product distilled from reaction mixture at 1 mmHg as it formed. ‖ After trapping as a cycloadduct (m.p. 118–120 °C) with diphenylisobenzofuran. ** After trapping with diphenylisobenzofuran (m.p. 128–130 °C). †† After trapping with diphenylisobenzofuran (m.p. 63–65 °C); this showed δ_H 7.2–7.8 (14 H, complex), 3.64 (3 H, s), 3.04 (1 H, d, J 6.1), 2.73 (1 H, d, J 6.1). ‡‡ After trapping as a cycloadduct (m.p. 148–150 °C; lit.,[7] 148–148.5 °C) with diphenylisobenzofuran. Product identical (NMR) with that reported.[7] §§ After trapping with diphenylisobenzofuran (m.p. 160–162 °C) (see M. S. Baird, H. L. Fitton, W. Clegg and A. McCamley, *J. Chem. Soc., Perkin Trans. 1*, 1993, 321).



mmol) and diethyl phosphite (0.28 g, 2.04 mmol) at 0–5 °C. The reaction mixture was allowed to reach 20 °C and stirred at that temperature for 20 min, when TLC showed that no starting material remained. The residue was placed directly on a silica gel column and eluted with light petroleum (b.p. 30–40) to give 1-bromo-2-octylcyclopropene (0.114 g, 96%) as a colourless oil which was identical (^{1}H NMR) with an authentic sample.[1]

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