

## Reaction of Allyl Bromides with Bromoform and Base under Phase Transfer Conditions

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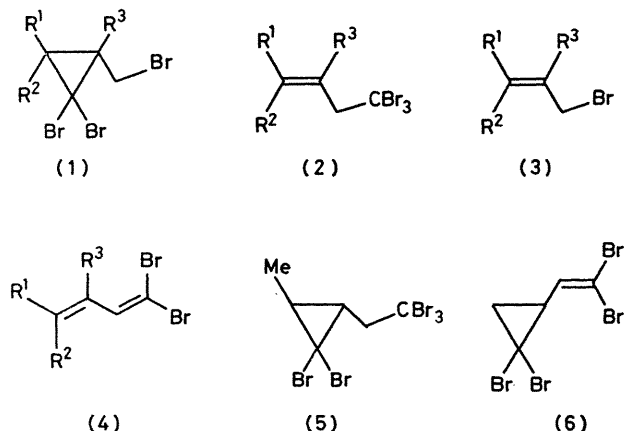
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**Summary** The reaction of allylic bromides with bromoform and aqueous base under phase transfer conditions is strongly dependent on the catalyst; when benzyltriethylammonium chloride is used, the major primary product is a 4,4,4-tribromobut-1-ene.

THE reaction of haloforms with strong aqueous base in the presence of a phase transfer catalyst leads to the trihalogenomethyl anion, which may lose a halide ion to produce the

corresponding dihalogenocarbene. Trapping of the latter by alkenes provides a convenient route to dihalogenocyclopropanes, though with alkenes substituted by electron withdrawing groups there is a delicate balance between dihalogenocyclopropane formation and trapping of the trihalogenomethyl anion by Michael addition, depending on other substituents.<sup>1</sup> In the presence of an allylic halide, trapping of the dihalogenocarbene can lead to useful yields of dihalogenocyclopropanes, *e.g.* (1); thus

adducts have been obtained from allylic chlorides with  $\text{CCl}_2$ ,  $\text{CFCl}$ , and  $\text{CBr}_2$ ,<sup>2</sup> and from allylic bromides with  $\text{CCl}_2$  and  $\text{CBr}_2$ .<sup>3</sup> A number of catalysts have been used for these reactions, but we now report that the products can be extremely dependent on the nature of the catalyst, and that under suitable conditions a useful alternative reaction leading to 4,4,4-tribromobut-1-enes (**2**) results.



Treatment of 2-methylallylbromide (**3**;  $\text{R}^1 = \text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{Me}$ ) with a small excess of bromoform and a large excess of concentrated NaOH in the presence of cetrimide (cetyltrimethylammonium bromide) led to a single product, (**1**;  $\text{R}^1 = \text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{Me}$ ) (40%) [ $\delta$  3.6 (s, 2H), 1.65 (s, 2H), and 1.6 (s, 3H)], in 18 h at 25 °C. However, when the cetrimide was replaced by TEBA (benzyltriethylammonium chloride), the reaction followed a completely different course, to produce (**2**;  $\text{R}^1 = \text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{Me}$ ) (38%) [ $\delta$  5.2 (br. s, 2H), 3.8 (s, 2H), and 2.1 (s, 3H)]; this has apparently arisen by nucleophilic substitution of bromide ion by tribromomethyl anion.<sup>4</sup>

The latter reaction was also observed when allyl bromide,<sup>†</sup> 4-bromo-2-methylbut-2-ene, and 4-bromobut-2-ene were treated with  $\text{CHBr}_3$ -aq. NaOH in the presence of TEBA, the corresponding tribromomethyl derivative (**2**) being isolated in each case (50, 58, and 40% respectively). Minor amounts of the dienes (**4**) were obtained in the first two cases, while in the last case the pentabromide (**5**) was observed at high conversions. Compounds (**4**) presumably arise by dehydrobromination of the primary products (**2**); this process was indeed observed when (**2**;  $\text{R}^1 = \text{R}^2 = \text{Me}$ ,

$\text{R}^3 = \text{H}$ ) was stirred with aq. NaOH-TEBA for prolonged periods at 25 °C or for 4 h at 55–60 °C. Compound (**5**) can also be obtained by reaction of (**2**;  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{R}^3 = \text{H}$ ) with  $\text{CHBr}_3$ -aq. NaOH-TEBA.

The marked catalyst dependence of the methylallyl bromide reaction above was also observed with other halides. Tetrabutylammonium bromide behaved in a very similar manner to TEBA, leading to formation of tribromomethyl derivatives (**2**;  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ , 37%) and (**2**;  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{R}^3 = \text{H}$ , 40%) from the corresponding bromide (**3**). Cetrimide, however, generally led to the dibromocyclopropanes (**1**), though the reactions were often much more complex. In particular the reaction of allyl bromide led to (**2**) and (**6**) as well as the adduct (**1**), and the relative yields were very dependent on the exact reaction conditions; presumably the products, and particularly (**2**), undergo further reactions under these conditions and product ratios will depend on the stage at which the reaction is stopped. The possible complexity of these reactions is also illustrated by the reaction of 4-bromo-2-methylbut-2-ene in the presence of cetrimide when an apparent hydrolysis to dimethylallyl alcohol (42%) occurs to the exclusion of formation of (**2**) or (**1**); compound (**1**), however, is formed when hydroxyethylbenzyltrimethylammonium chloride is used as the catalyst.

The application of the substitution by  $\text{CBr}_3$  to secondary bromides seems less promising, 3-bromocyclohexene giving complex products including only a low yield (ca. 12%) of 3-tribromomethylcyclohexene. Moreover, the reaction does not seem to be successful when either the haloform or the bromide are replaced by their chlorine analogues. The reaction of allylbromide with chloroform-aq. NaOH-TEBA is reported to lead to 1,1-dichloro-2-bromomethylcyclopropane.<sup>3†</sup> The reaction of allylchloride with bromoform-aq. NaOH-TEBA for 18 h at 25–40 °C was complex, while 2-methylallyl chloride gave 1,1-dibromo-2-chloromethyl-2-methylcyclopropane; addition of sodium iodide to the latter reaction apparently gave (**2**;  $\text{R}^1 = \text{R}^2 = \text{H}$ ,  $\text{R}^3 = \text{Me}$ ) to the exclusion of the cyclopropane, but complex halide exchange reactions led to additional side products, including iodoform, and precluded purification of the bromide.

These reactions are clearly more complex than had been thought and further studies to elucidate the nature of different catalytic effects and to define more clearly the limits of synthetic applications are under way.

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<sup>†</sup> Added in proof. Since submitting this paper we have become aware of a recent paper (N. N. Labeish, E. M. Kharicheva, T. V. Mandel'shtam, and R. R. Kostikov, *Zhur. org. Khim.*, 1978, **14**, 878; *Chem. Abs.*, 1978, **89**, 23809) in which (**2**,  $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ ) was reported as a minor product from this reaction under unspecified conditions.

<sup>‡</sup> Under conditions similar to those reported we have also observed the formation of allyl chloride (37%), while the use of hydroxyethylbenzyltrimethylammonium bromide leads to both the dichlorobromide and 1,1-dichloro-2-chloromethylcyclopropane.

<sup>1</sup> M. Makosza and M. Ludwikow, *Angew. Chem. Internat. Edn.*, 1974, **13**, 665; M. Makosza and I. Gajos, *Bull. Acad. Polon. Sci., Ser. Sci. chim.*, 1972, **20**, 33; E. V. Dehmlow, *Annalen*, 1972, **758**, 148; M. R. Barlet, *Compt. rend.*, 1974, **278C**, 621; L. Sydnes and L. Skattebol, *Tetrahedron Letters*, 1975, 4603.

<sup>2</sup> M. Makosza and M. Fedorynski, *Synthetic Comm.*, 1973, **3**, 305; R. F. Boswell and R. G. Bass, *J. Org. Chem.*, 1975, **40**, 2419; W. Kraus, G. Klein, H. Sadlo, and W. Rothenwöhler, *Synthesis*, 1972, 485; M. Schlosser and L. V. Chau, *Helv. Chim. Acta*, 1975, **58**, 2595.

<sup>3</sup> T. Hiyama, H. Sawada, M. Tsukanaka, and H. Nozaki, *Tetrahedron Letters*, 1975, 3013; M. Makosza and M. Fedorynski, *Synthesis*, 1974, 274.

<sup>4</sup> Trichloromethyl Grignard reagents are reported to undergo low temperature coupling with allyl bromide to produce 4,4,4-trichlorobut-1-ene: J. Villieras, *Bull. Soc. chim. France*, 1967, 1520.