A Convenient Transformation of Benzyl Bromides into (2-Bromoethynyl)benzenes

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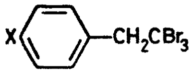
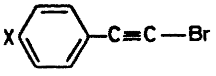
Summary Prolonged reaction of benzyl bromides with bromoform–aqueous NaOH in the presence of a phase transfer catalyst leads to (2-bromoethynyl)benzenes.

WE have recently reported that reaction of allylic bromides with aqueous NaOH–$CHBr_3$–TEBA (TEBA = triethylbenzylammonium chloride) in a two-phase system can lead to useful yields of 4,4,4-tribromobut-1-enes, apparently by nucleophilic substitution of bromide by the tribromomethyl anion.[1] This suggested a number of related synthetic applications.



(1)



(2)

The reaction of benzyl chloride with aqueous NaOH–$CHBr_3$–TEBA is reported to lead to low yields of (2,2,2-tribromoethyl)benzene (**1**, X = H).[2] However, using benzyl bromide with cetrimide as catalyst we have obtained (**1**, X = H) in reasonable yield (59%) in 100 h at 25 °C. Furthermore, the substituted tribromides (**1**, X = Me and Br) were obtained from the corresponding bromides (57 and 71%) by reaction with NaOH–$CHBr_3$–TEBA for 15 min at 60 °C and for 6 h at 45—55 °C, respectively. If the reactions were allowed to continue after formation of the tribromides, these were slowly consumed and replaced by a single major product, the acetylene (**2**); monitoring did not show any appreciable build up of the corresponding $\beta\beta$-dibromostyrenes during the reactions.† In this way we have obtained (**2**, X = H)[3] (60%), (**2**, X = Me)[3] (53%),‡ and (**2**, X = NO_2) (58%)[3],§ in 48 h at 60—70 °C, 7·5 h at 60—80 °C, and 20 h at 35 °C (in CH_2Cl_2 solvent), respectively, using TEBA as catalyst, and (**2**, X = H) (58%) in 40 h at 100 °C using tetrabutylammonium hydroxide as catalyst. Conventional syntheses of bromoethynylbenzenes generally involve bromination of the corresponding ethynylbenzene;[3] the present reaction may offer a useful alternative.

This sequence can also be applied to 2-substituted benzyl bromides. Thus 2-methylbenzylbromide is converted into 2-methyl-1-(2,2,2-tribromoethyl)benzene (53%) in 7 h at 40—60 °C and into 1-(2′-bromoethynyl)-2-methylbenzene (53%)‡ in 2·5 h at 80 °C using aqueous NaOH–$CHBr_3$–TEBA. However, it only appears to work well for primary benzyl bromides and bromoform. Thus benzyl chloride was unchanged after reaction with $CHCl_3$–aqueous NaOH at 60—70 °C for 20 h in the presence of TEBA (although the chloroform was consumed) and benzyl bromide was largely unchanged by similar treatment, although some benzyl chloride was formed, presumably by halide exchange.¶ (1-Bromoethyl)benzene was slowly converted into 1-phenylethanol and minor products over 7 days at 50 °C with NaOH–$CHBr_3$–TEBA; this was surprising in view of the known conversion of alcohols into bromides by this reaction system.[4] Indeed, 1-phenylethanol was partially converted into the bromide with NaOH–$CHBr_3$–TEBA, and this reaction is clearly very dependent on relative reagent concentrations. However, when primary benzylic alcohols were treated in this way they were transformed first to the benzyl bromide and then to the tribromomethyl derivative (**1**) or the acetylene (**2**), albeit in low yield. In this way (**1**, X = H) (17%) and (**1**, X = OMe) (19%) were obtained from benzyl alcohol and 4-methoxybenzyl alcohol in 20 h and 8 days, respectively at 25—35 °C in CH_2Cl_2, and (**2**, X = Me) was obtained from 4-methylbenzyl alcohol (24%) in 4·5 h at 50—55 °C.

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† Under these conditions 4,4,4-tribromobut-1-enes are dehydrobrominated to 1,1-dibromobutadienes, see ref. 1.

‡ Minor products which are apparently dimers of the acetylenes were also observed; these are under further investigation.

§ In this case dehydrobromination of the intermediate (**1**, X = NO_2) to (**2**, X = NO_2) competed with the formation of the former from 4-nitrobenzylbromide even at 25 °C and the maximum conversion into (**1**) was *ca.* 60% by n.m.r. spectroscopy.

¶ The reaction cannot be extended to (2-bromoethyl)benzene, which on treatment with aqueous NaOH–$CHBr_3$–TEBA is essentially unchanged after 4 days at 60 °C.

[1] M. S. Baird, A. G. W. Baxter, B. R. J. Devlin, and R. J. G. Searle, *J.C.S. Chem. Comm.*, 1979, 210.
[2] M. Makosza, *Pure Appl. Chem.*, 1975, **43**, 439; *Russ. Chem. Rev.*, 1977, 1151.
[3] G. Eglinton and W. McCrae, *J. Chem. Soc.*, 1963, 2295.
[4] W. P. Weber and G. W. Gokel, 'Phase Transfer Catalysis in Organic Synthesis,' Springer-Verlag, Berlin, 1977, and references therein.