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REACTIONS OF ORGANOBORANES WITH CHLORAMINE-T AND ITS ANALOGUES; SYNTHESIS OF N-SUBSTITUTED SULPHONAMIDES

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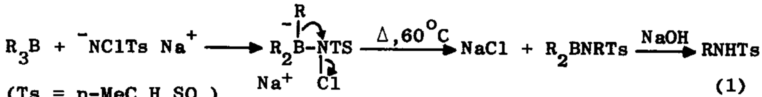
Organoboranes are known to react with chloramine (NH_2Cl) or hydroxyamine-O-sulphonic acid to give aminoboranes which may be hydrolysed to primary amines.[1] Secondary amines are available from organoboranes by reaction with organic azides[2] or with the O-2,4-dinitrophenyl derivative of chlorohydroxyamine,[3] although the latter reaction has been established to date on only one example. There are as yet no examples of similar reactions leading to nitrogen compounds possessing substituents other than H or alkyl groups attached to nitrogen. We now present such a reaction.

Chloramine-T ($Na^+\ {}^-NClSO_2C_6H_4Me$) is a readily available material which, by analogy with the reactions referred to above, should react with organoboranes to yield N-substituted toluenesulphonamides (1) (Equation). Indeed, when anhydrous chloramine-T is reacted with a trialkylborane in THF for 6 h. at 55-60°C, there is a slow precipitation of sodium chloride and hydrolysis then gives the expected sulphonamides in good yields. (1, R = Hex^n, 84%; Oct^n, 80%; cyclopentyl, 74%; cyclohexyl, 72% using excess chloramine-T; benzyl, 69%; all after purification). Commercially available chloramine-T trihydrate gives entirely comparable results to the anhydrous material. N-Hexyl derivatives of benzenesulphonamide and 4-methyl-3-nitrobenzenesulphonamide have also been obtained from the hydrated forms of the corresponding chloramine derivatives by reaction with trihexylborane.



$$R_3B + {}^{-}NClTs\ Na^{+} \longrightarrow R_2\overset{R}{\overset{|}{\bar{B}}}-\underset{Cl}{\underset{|}{N}}Ts\ \ Na^{+} \xrightarrow{\Delta,60^{\circ}C} NaCl + R_2BNRTs \xrightarrow{NaOH} RNHTs$$

(1)

($Ts = p\text{-}MeC_6H_4SO_2$)

In all cases, only one of the alkyl groups initially attached to boron is transferred during the reaction, and use of a threefold excess of chloramine-T does not alter this situation. Furthermore, the reaction with dicyclohexyl-n-octylborane gives a mixture of sulphonamides which indicates that the cyclohexyl group migrates approximately three times more readily than the n-octyl group. Preferential migration of the ring carbon atoms of 9-octyl-9-borabicyclo[3.3.1]nonane is also observed. Such preferential migration of a secondary group in non-radical reactions of organoboranes is unusual, but has been observed previously.[4] 3,6-Dimethyl-1-octylborepane undergoes competitive migration of both groups in almost statistical proportions, and we are still seeking an alternative way of overcoming this limitation to quantitative utilisation of alkyl residues.

The new reaction sequence is a viable alternative to traditional routes to substituted sulphonamides. These involve either the reaction of sulphonyl chlorides with excess amine or the rather restricted alkylation of primary sulphonamides,[5] which is generally unsuccessful for derivatives such as N-cyclohexylsulphonamides. Many analogues of chloramine-T are available[6] and a study of their reactions should considerably extend the scope of the present process. Since sulphonamides can be cleaved by a variety of processes to yield the constituent amines,[7] this reaction is also a formal synthesis of amines.

The following procedure for preparation of N-(1-hexyl)-toluenesulphonamide is representative. A 100 ml three-necked flask equipped with a bent side arm,[8] septum-capped stopcock inlet, nitrogen/vacuum inlet, and magnetic follower was charged with anhydrous chloramine-T (1.25 g, 5.5 mmol) in the side arm, evacuated, and filled with nitrogen. Into the flask was put THF (5 ml), borane-THF (4.3 ml of a solution 1.18M in BH_3, 5 mmol) and hex-1-ene (1.9 ml, 15 mmol), and the mixture was stirred at 20°C for 1 h. The side arm was twisted so as to tip the chloramine-T into the flask and stirring was maintained. After the initial vigorous reaction had subsided, the mixture was heated to *ca.* 58°C and maintained 6 h. with stirring. The mixture was cooled to 20°C, 4M NaOH (5 ml) was added, and the whole was stirred overnight. The product was extracted into diethyl ether, dried, evaporated, and taken into dichloromethane leaving R_2BOH compounds undissolved. The solvent was evaporated, and the product was washed with the minimum quantity of pentane to remove traces of hexan-1-ol, leaving essentially pure N-hexyltoluene-4-sulphonamide (1.08 g, 84%), m. 59.5°C (after crystallisation from a mixture of dichloromethane and pentane); lit.[9] 60°C.

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