Bromonitromethane, a Versatile Electrophile: Reactions with Feebly Basic Nucleophiles

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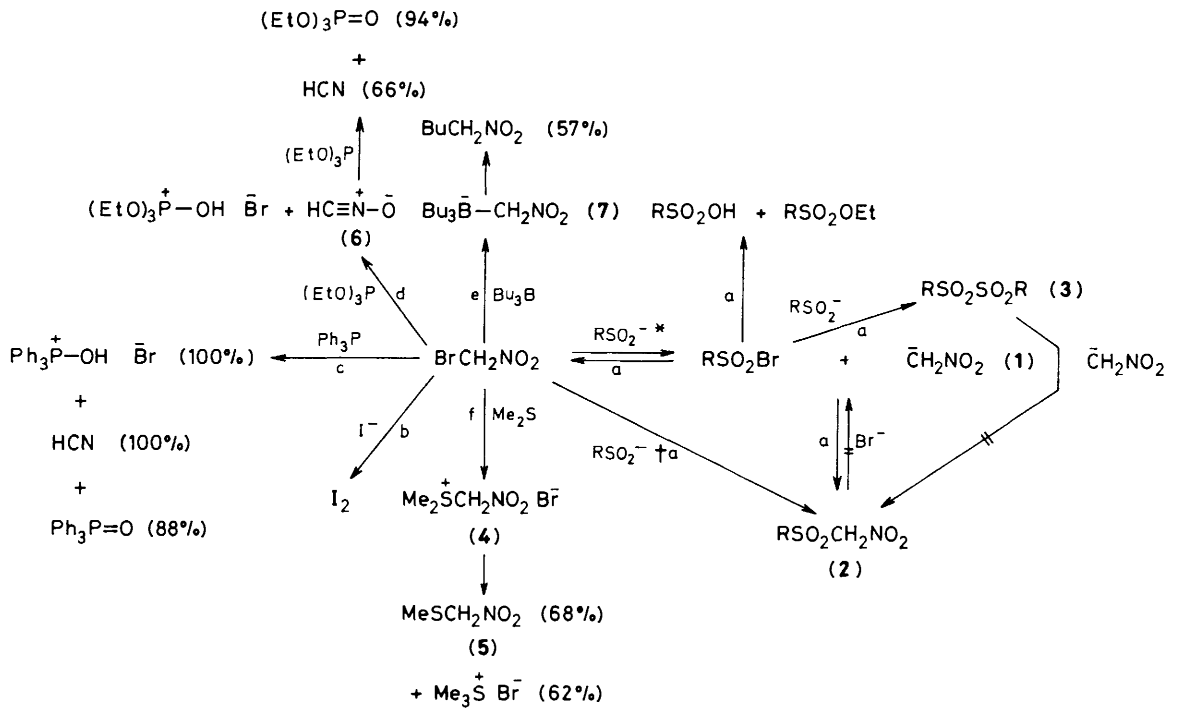
Bromonitromethane reacts with feebly basic sulphur, phosphorus, and halogen nucleophiles at bromine or at carbon; the anion of bromonitromethane reacts with tributylboron to give 1-nitropentane.

In the preceding communication[1] the rapid reaction of thiolate ions with bromonitromethane was shown to give disulphides; the pK_a's of nucleophile (conjugate acid) and electrophile in this case are comparable, and a considerable portion of the electrophilic substrate would be present as the conjugate base. In this communication we report reactions with much more



Scheme 1. *Solvents*: a, EtOH–H_2O (50:50 v/v); b, MeOH; c, C_6H_6; d, Et_2O; e, THF; f, MeCN. * Attack at Br; † attack at C.

feebly basic nucleophiles; three out of the five atoms of the molecule show electrophilic character (Scheme 1).

Toluene-*p*-sulphinate ion, in 50% aqueous ethanol, reacts to give an equilibrium mixture of sulphonyl bromide and nitronate ion (**1**), the former reacting with the latter to regenerate bromonitromethane and to give nitromethylsulphone (**2**) irreversibly notwithstanding the poor *C*-nucleophilicity of (**1**).[2] This product is not formed from α-disulphone (**3**) and nitronate ion (**1**). This result is in accord with the observation of quantitative formation of nitromethane from bromonitromethane and tetrabutylammonium benzenesulphinate.[3] The sulphonyl halide is also intercepted by sulphinate ion to give α-disulphone and by water and ethanol to give sulphonic acid and its ethyl ester. A closely similar product distribution is found when sulphonyl bromide and nitronate ion (**1**) are the starting materials showing that equilibrium is established rapidly by comparison with the slow irreversible leakages to other products. The course of the reaction thus resembles that with thiolates[1] but the sulphonyl bromide is very much less electrophilic than sulphenyl bromide and the sulphinate ion much less nucleophilic than the thiolate ion.

Dimethyl sulphide reacted very slowly with bromonitromethane to give the sulphide (**5**) and trimethylsulphonium bromide, presumably *via* dealkylation of the salt (**4**). Other alkyl methyl sulphides bearing β-substituents such as CN (5 days at 120 °C, neat) and OH failed to react. Attack at carbon even for a very feebly basic nucleophile is poorly favoured. Iodide ion, another feebly basic nucleophile, gives iodine presumably *via* iodine bromide; nitromethane is obtained after buffering reaction mixtures.

Products from reactions with phosphorus nucleophiles in benzene, which again are very feebly basic, probably involved attack at bromine as shown in Scheme 1, similar pathways being followed by triphenylphosphine and by triethyl phosphite, with reagents in a 2:1 mole ratio to bromonitromethane. Hydrogen cyanide formed probably arises from the oxide (**6**). Trippett, Walker, and Hofmann have reported[4] formation of hydroxyiminomethyltriphenylphosphonium bromide from bromonitromethane and triphenylphosphine in benzene at 0 °C. We have obtained a product (10%) with the same properties as those described earlier but we cannot establish the presence of a $\geqslant P^+–CH=$ function by n.m.r. Attack at bromine by phosphorus and reaction of nitronate ion (**1**) with the bromophosphonium bromide formed could account for formation of the products *via* (**6**). Our results for triethyl phosphite also differ from those of Arbuzov *et al.*[5] who reported formation of triethyl phosphate (55%), ethyl bromide (49%), and ethylene together with other gaseous products, when the products (not stated) of the initial reaction at 20 °C were kept at 160 °C.

Tributylborane reacted in tetrahydrofuran (THF) with the anion of bromonitromethane, generated by addition of 2,6-di-t-butylphenoxide ion,[6] to give 1-nitropentane (57%). This reaction has potential for the alkylation of nitroalkanes and is to be further investigated; the reaction presumably proceeds by migration–displacement in (**7**). In this case, of course, the electrophilic atom is hydrogen. Bromonitromethane was recovered in high yield from methanolic sodium methoxide, conditions which would effect virtually quantitative conversion of the nitro-compound into its conjugate base, inert to further reaction.

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