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A REINTERPRETATION OF THE TRANSFORMATION OF BROMONITROCOMPOUNDS TO KETONES

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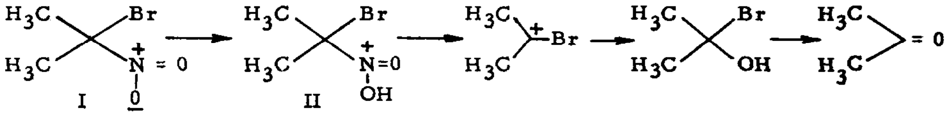
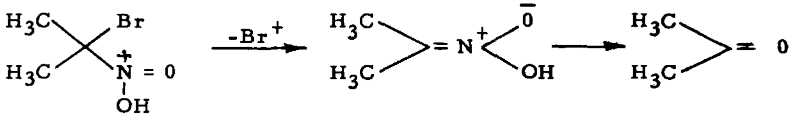
Recently[1] we made the observation, on the basis of isolation of 2-bromo-p-cymene from 2-bromo-2-nitrocamphane, that bromonitrocompounds could readily lose the nitro group on treatment with sulphuric acid. Subsequently and independently Wassmundt, Gilleo and Christiano[2], have proposed the loss of nitro group as the primary step in the transformation of bromonitrocompounds to carbonyl compounds:



Our own studies however, indicate that the carbonyl compounds arise not through the loss of the nitro group, but through loss of elements of Br^+, followed by transformations closely related to the Nef reaction[3]:



This alternate possibility came to our notice in an altogether fortuitous manner. Reaction of bromonitrocyclopentane[4] in excess hexane-sulfuric acid gave as one of the very minor products (<1%), solid mp 87°, which was identified as p-dibromobenzene and its genesis traced to minor amounts of benzene present in the hexane used. This result suggested the presence of brominating species in the reaction mixture and was soon confirmed with the isolation of p-dibromobenzene in 63% yields, by shaking for 5 hr. a mixture of 2-bromo-2-nitropropane (I) (0.02 mole), bromobenzene (0.04 mole) and sulfuric acid (30 ml, 98%), followed by dilution and steam distillation. p-Dibromobenzene crystallizes in the condenser and the acetone present in the distillate was estimated as its 2,4-dinitrophenylhydrazone (52%). The yield of acetone obtained in this experiment (52%), that reported (60%)[2] and the yield of p-dibromobenzene (63%) are all comparable implying that the ketone formation takes place predominantly or exclusively through the loss of Br^+ from the protonated intermediate II. The yield of acetone remains nearly the same in all the experiments with 2-bromo-2-nitropropane and is unrelated to the bromination step. For example when the highly electrophilic nitrobenzene was used, although no bromination took place, the yield of acetone was unchanged (48%); further, delayed addition of bromobenzene gave a poor yield (9%) of p-dibromobenzene, whilst not affecting the yield of the ketone (49%). Blank experiments showed that sulfuric acid was essential for the bromination, molecular bromine was not effective and when aromatic substitution is absent bromine is produced[2]. All these observations could be accommodated on basis of the intermediacy of $BrOH_2^+$, which could effect aromatic halogenation[5] or could give bromine[6]. The unlikely possibility that the brominating species results from sulfuric acid oxidation of HBr, expected on the basis of the mechanism proposed[2], was proved untenable because of virtual lack of formation of product (0.6%) when KBr was gradually introduced into bromobenzene-sulfuric acid. Aromatic bromination with bromonitro compounds-sulfuric acid appears to be general and the results from some bromonitro compounds are listed below:

bromonitro compound[4]	aromatic substrate	bromocompound (yield %)
bromonitropropane	bromobenzene	p-dibromobenzene (63)
	diphenyl	4,4'-dibromodiphenyl (24)
bromonitrocyclohexane	bromobenzene	p-dibromobenzene (50)
bromonitrocyclopentane	bromobenzene	p-dibromobenzene (31)

Sulfuric acid transformations of a variety of bromonitro compounds along with their corresponding nitronic acid salts are being examined with chemical and analytical probes to further understand the behaviour of the protonated intermediates and to delineate the fate of the bromine-free species.

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