Novel Aromatic Bromination Using BrF Prepared Directly from the Corresponding Elements

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BrF, made directly from the corresponding elements, may be used without any catalyst as an efficient electrophilic brominating agent in its reactions with activated and deactivated aromatic rings.

Aromatic bromination is a well established procedure which has been known from the beginnings of modern organic chemistry and is described in every elementary text book. However, such brominations when applied to non-activated systems have been confined either to a diazotised aniline derivative or to electrophilic bromination, mainly with Br_2, in the presence of Friedel–Crafts catalysts such as $AlCl_3$ or $FeBr_3$. These methods have some obvious limitations including the employment of large amounts of water-sensitive catalysts which create disposal problems on an industrial scale.

In connection with our work on fluorine it occurred to us that BrF, which is easily prepared *in situ*, could be an excellent source of a highly polar bromine derivative. Bromine monofluoride was prepared by passing diluted fluorine† (about 10% F_2 in N_2) through a cold (−75 °C) suspension of bromine in $CFCl_3$.[1] The formation of BrF is almost quantitative as can be deduced, for example, from some of its reactions with alkenes.[1] In its reactions with aromatic compounds, however, it tended to split homolytically, even at −75 °C. This resulted in indiscriminate attack of the organic substrate so no specific halogenation could be detected. When, however, a small amount of a polar, proton-donating solvent such as an alcohol was added, the radical formation was suppressed and smooth reaction of ionic type took place.[1]

Thus, to a suspension of BrF (50—60 mmol) in $CFCl_3$ at −75 °C, ethanol (60—70 mmol) was added, resulting in a clear solution. A solution of an activated aromatic substrate, such as toluene, anisole, *etc.*, in a small amount of $CHCl_3$ at −75 °C was added to 5—10% excess of the BrF solution at −75 °C. Anisole was brominated quantitatively (*para*:*ortho* 4:1). Toluene was also monobrominated in >90% yield (*para*:*ortho* 1:1). When the *ortho* position is sterically hindered, as in the case of t-butylbenzene, only *para* bromination takes place, in 90% yield. With less activated aromatic rings, such as phenyl acetate or bromobenzene, quantitative *para*-bromination was observed. In all these cases full conversion of the starting material was achieved in 5—15 min.

The efficiency of this reaction is even better demonstrated with aromatic rings which are deactivated towards electrophilic reactions. These react with BrF at −45 °C with reaction times ranging from a few minutes up to 1 hour. The inherent deactivation did not affect the efficiency of the reaction and essentially pure *meta*-bromo derivatives were obtained in very high yields. Thus ethyl benzoate was converted into *m*-bromoethyl benzoate in 95% yield. Sensitive groups such as aldehydes were not affected by the reagent and benzaldehyde was transformed to *m*-bromobenzaldehyde in >90% yield. Even *m*-dinitrobenzene was brominated in 45 min without any catalyst, forming the expected 1,3-dinitro-5-bromobenzene in 93% yield.‡

The main advantage of this new brominating method is that one does not have to employ the usually large amounts of strong Lewis acid catalyst even with highly deactivated rings. In addition the reaction is fast, efficient, does not require high temperatures and can accommodate the presence of sensitive groups. Finally, since fluorine in bulk is cheaper than bromine, this method has the advantage of using the two atoms of the bromine molecule without losing one of them in the form of HBr.

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References

1 S. Rozen and M. Brand, *J. Org. Chem.*, 1985, **50**, 3342; 1986, **51**, 222.

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† **Caution:** Reactions with F_2 should be conducted with care and in a well ventilated area. If elementary precautions are taken, however, the work with fluorine and its derivatives is safe and relatively simple. In the past, we have never had any accidents while working with it.

‡ It is advisable to trap the liberated HF using lime producing harmless CaF_2 and water.