HALONITROMETHYLATION OF BENZENE AND ITS DERIVATIVES

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The reaction of aromatic compounds with xenon difluoride in the presence of catalytic amounts of acid gives the products of aromatic ring fluorination [1]. We are the first to show that xenon difluoride reacts with aromatic hydrocarbons in an excess of a fluorine-containing halonitroacetic acid to form the products of fluoronitromethylation of the aromatic ring.

$$O_2NCFR{-}COOH + {}^1/_2\,XeF_2 + PhR' \xrightarrow{\begin{array}{l}R=Cl\\ R=F\end{array}} \begin{array}{l} O_2NCFCl{-}PhR' + {}^1/_2\,Xe + HF + CO_2 \\ \quad (I){-}(III) \\ O_2NCF_2PhR' + O_2NCF_2COOPhR' + CO_2 + {}^1/_2\,Xe + HF \\ \quad (VI){-}(VI)\end{array}$$

R = Cl, R′ = H (I); R = Cl, R′ = CH_3(II); R = Cl, R′ = F (III); R = F, R′ = CH_3(IV); R = F, R′ = F (V); R = F, R′ = H (VI)

The reaction was carried out in CCl_4 at 10-15°C. In order to avoid the formation of fluorination products, the reactions were carried out with a constant excess of the halonitroacetic acid. The structure of the reaction products was found to depend on the substituent R in the starting halonitroacetic acid. Thus, when R = F, phenyl esters of difluoronitroacetic acid are formed in addition to (IV)-(VI) as indicated by ^{19}F NMR and IR spectroscopy and mass spectrometry. The formation of these esters is likely related to the great stability of the intermediate difluoronitroacyl radical. Products (II)-(V) are mixtures of o-, m-, and p-isomers in ~1:1:1.5 ratio as indicated by the integral curve of the ^{19}F NMR spectrum. The yield of products (I)-(VI) was 35-65%. The structures of the synthesized compounds were established by IR, ^1H and ^{19}F NMR spectroscopy and mass spectrometry.

LITERATURE CITED

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