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INTRODUCTION OF THE HALONITROMETHYL FRAMEWORK INTO AROMATIC RINGS VIA A XeF_2 MEDIATED RADICAL PROCESS

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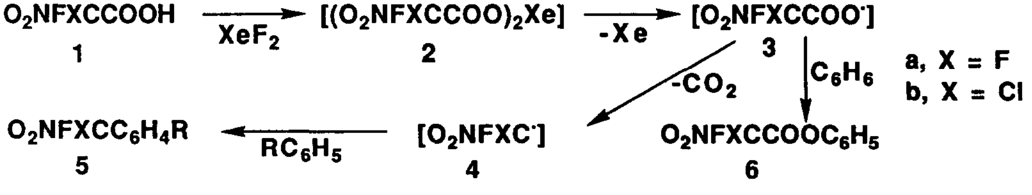
Summary. *Reaction of difluoronitro- and fluorochloronitroacetic acids with aromatic substrates in the presence of XeF_2 results in alkylation of the aromatic ring by the $O_2NF_2C\cdot$ and $O_2NFClC\cdot$ radicals.*

Xenon difluoride is a convenient reagent for the fluorination of organic compounds[2]. It has also been demonstrated that XeF_2 can be used for the introduction of a CF_3 group into aromatic rings *via* a radical process of oxidative decarboxylation of CF_3COOH[3a,4]. However, the lack of selectivity of the intermediate radical precludes the potential synthetic application of this reaction. Recently we have found that NO_2-containing radicals (e.g., $O_2NFClC\cdot$) generated from halonitroacetic acids are extremely reactive, and easily undergo a variety of useful transformations[3b,c]. Herein we report the reaction of XeF_2[5] and halonitroacetic acids in the presence of aromatic compounds in order to delineate the scope and limitations of this potentially important synthetic transformation of an aromatic ring.

Reaction of difluoronitroacetic acid with XeF_2 in benzene[6] gave α-nitro-α-halotoluene **5a** as the major product, along with ester **6** as a by-product. The analogous reaction of fluorochloronitroacetic acid in the presence of an aromatic substrate gave **5b** as the major product. A likely mechanism involves intermediate formation of xenon biscarboxylate **2**[7] as a precursor of radicals **3** and **4**, which concequently alkylate the benzene ring.



Compound **5b** was obtained as a mixtures of o-, m-, and p-isomers in a ratio of 1:1:1.5, as determined by ^{19}F NMR data. The o-isomer of **5b** (R = F, $J_{F\text{-}F}$ = 15.5 Hz) was isolated in pure form by preparative gas chromatography. Fluorochloronitromethane, the result of the haloformic degradation of acid **1b**, was identified as the major side product in these reactions.

In order to establish the polar character of radical **4b** competition experiments were carried out between monosubstituted benzenes and benzene. The following relative rates were observed: $C_6H_5CH_3 : C_6H_6 : C_6H_5F : C_6H_5Cl : C_6H_5NO_2 : C_6H_5CF_3$; 2.5 : 1.0 : 0.5 : 0.35 : 0.08 : 0.01. These data clearly establish the unusual electrophilic nature of radical **4b**[8]. Moreover, in analogy with other electrophilic radicals **4b** reacts exclusively with the aromatic ring and not the side chain of toluene.

In conclusion, the XeF_2 mediated oxidative decarboxylation of halogen and nitro substituted carboxylic acids in the presence of aromatic compounds gives products of radical substitution and can be regarded as a novel method of $C\text{-}C_{Ar}$ bond formation.

References and Notes

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6. A typical procedure is: To a stirred solution of 3.14 g (0.02 mol) of **1b** in 3 ml of CCl_4 and 3 ml of C_6H_6 at 15°C 2.54 g of XeF_2 was added in portions. The reaction mixture was washed with 3% aqueous $NaHCO_3$ followed by washing with water. Work-up and distillation *in vacuo* gave 1.88 g (33%) of **5b**. Other yields were **5a** (38%), **6** (15%), **5b** ($R = CH_3$, 43%), and **5b** ($R = F$, 31%).
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