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SHORT COMMUNICATION

FLUORINATION WITH XENON DIFLUORIDE. PREPARATION OF ARYLIODINE/III/DIFLUORIDE[*]

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The addition of chlorine to olefinic double bonds using phenyliodine/III/dichloride as a halogenating agent has received attention from several groups of workers [1-4]. The corresponding aryliodine/III/difluorides received much more limited attention as fluorinating agents, possibly because of the difficulty involved in their preparation and storage. Three methods are of particular interest for the preparation of aryliodine/III/difluorides. The first is the method of Dimroth and Bockemüller [5] or the modified one of Garvey [6] et al., in which the appropriate aryliodoso compound is treated with 46 % HF in acetic acid. The method of Carpenter [7] involves a one-step reaction of mercuric oxide and aqueous hydrofluoric acid with the aryliodine/III/dichloride in methylene chloride. The methylene chloride solution is then used directly for fluorination. The third procedure [8] involves the electrolysis of an acetonitrile solution of silver/I/fluoride and iodobenzene.

The recent reported synthesis of methyliodine/III/difluoride in the reaction of xenon difluoride with an excess of methyl iodide [9] makes this potential fluorinating agent readily available [10].

We developed a similiar method for the synthesis of various aryliodine/III/difluorides, using xenon difluoride as fluorinating agent in methylene chloride

$$X\text{-}\Phi\text{-}I + XeF_2 \xrightarrow[CH_2Cl_2]{HF} X\text{-}\Phi\text{-}IF_2 + Xe$$

X : H, m-OCH_3, p-OCH_3, m-Cl, p-Cl, m-NO_2

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solution in the presence of anhydrous hydrogen fluoride at room temperature. The reaction with p-methoxiiodobenzene was completed in 45 min., while in the case of m-nitro, three hours were needed. The most promising, due to its stability, solubility and separation from the products, seems to be m-chlorophenyliodine/III/difluoride.

The quantity of active fluorine was established by iodometry. 95 % of iodobenzene was converted to aryliodine/III/difluoride. We tested all synthesised aryliodine/III/difluorides by reaction with 1,1-diphenylethene, which resulted in formation of 1,1-difluoro-1,2-diphenylethane.

$$\Phi_2C = CH_2 + X\text{-}\Phi\text{-}IF_2 \xrightarrow[CH_2Cl_2]{HF} \Phi\text{-}CF_2\text{-}CH_2\text{-}\Phi$$

The substituted aryliodine/III/ difluorides offer the possibility of future studies on the reaction mechanism of fluorination with these reagents.

EXPERIMENTAL SECTION

I.r. spectra were recorded by using a Perkin Elmer 137 spectrometer, ^1H and ^{19}F n.m.r. spectra by a Jeol-JNM-PS-100 from CCl_4 solution with TMS and CCl_3F as internal standards. Mass spectra were taken by a CEC 21-110 spectrometer. T.l.c. separation was carried out on Merck Fertigplatten SiO_2.

Materials

Substituted iodobenzenes were prepared by known methods from corresponding aminoderivates and distilled before use. 1,1-diphenylethene was prepared by known methods [13] and distilled before use. Xenon difluoride was prepared by photosynthetic methods [11] and its purity was better than 99.5 %. Methylene chloride was purified [12] and stored over molecular sieves. Hydrogen fluoride of Fluka Purum quality was used.

Substituted iodobenzene/III/ difluorides

1.1 mmol of substituted iodobenzene was dissolved in methylene chloride (5 ml) at room temperature, anhydrous HF (1-3 mmols) was introduced into the reaction mixture and under stirring pure XeF_2 (1.1 mmol) was added. After a few seconds the colourless solution turned dark green and xenon gas was evolved. After 45 min. (for p-OCH_3 or 3 hr. for m-NO_2 derivate) gas evolution had ceased and reaction appeared to be complete. The solution was used for fluorination of olefins.

1.1-difluoro-1,2-diphenylethane

To a solution of the previously prepared substituted iodobenzene/III/ difluoride, 1 mmol of 1.1-diphenylethene was added under stirring at room temperature. After 2 hr. the reaction mixture was diluted with methylene chloride (15 ml), washed (10 ml of 5% aqueous $NaHCO_3$), dried (Na_2SO_4) and solvent was evaporated in vacuo. The crude product was separated by preparative t.l.c. and 1.1-difluoro-1.2-diphenylethane was isolated in a yield of 60 - 70 %. After crystallisation from pentane, the white crystals melted at 65 - 67°C, lit. [5] mp 66°C, n.m.r. (CCl_4) δ 3.3 (t, 2H, $-CH_2-$, J = 15 Hz) δ 7.2 (m, 10 H, Ph) δ - 96.75 (t, $PhCF_2-$).

Determination of active fluorine in substituted iodobenzene/III/ difluorides

To a solution of the previously prepared substituted iodobenzene/III/ difluoride, 50 ml of KI solution (9 g KI dissolved in 1 litre of a 1 : 4 mixture of methanol and water) and 1 ml of diluted HCl (1 : 1) was added. The reaction mixture was stirred in the dark and in an atmosphere of N_2 at room temperature for 6 hr. Liberated iodine was titrated by $Na_2S_2O_3$ (0.025 N). The results showed that the mixture included 1 mmol of active fluorine.

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