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SHORT COMMUNICATION

FLUORINATION WITH XENON DIFLUORIDE. PART V. REACTION WITH 1,4-DIHYDROXY AND 1,2-DIHYDROXY-4-t-BUTYLBENZENE*

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In our continued interest in the fluorination of organic molecules with XeF_2 [1-4] we have also studied the oxidation properties of XeF_2. N.Bartlett and F.O.Sladky [5] reported oxidation of iodine to iodine/V/fluoride. L.I.Nikolenko and coworkers [6] observed the oxidation of pentafluorophenol with XeF_2 in acetonitrile to corresponding $(C_6F_5)_2O_2$. The reaction with benzoic acid and derivates in the presence of benzene resulted in phenylbenzoates [7,8]. In the reaction of 1,2-dihydroxybenzene with XeF_2 R.Filler and coworkers [9] observed formation of 1,2-dihydroxy-4-fluorobenzene in a yield of 38%. Reaction with phenol resulted in a mixture of three fluorophenol-isomers, but 1,3-dihydroxybenzene gave a fluorinated product with unestablished structure. There was no evidence given for the oxidation of corresponding dihydroxybenzene derivates to quinones.

We now report the reaction of XeF_2 with 1,4-dihydroxy and 1,2-dihydroxy-4-t-butylbenzene in methylene chloride at 20°C. The reaction occurs immediately and results in formation of corresponding quinones in high yield.

Experimental Section

I.r. spectra were recorded by using a Perkin Elmer 257 spectrometer, and ^1H n.m.r. spectra by a Jeol JNM-PS-100 from $CDCl_3$ solution with TMS as internal standard. Mass spectra were taken on a CEC-21-110 spectrometer. T.l.c. separation was carried out on Merck Fertigplatten SiO_2.

Material

The dihydroxy compounds were obtained from commercial sources and purified to conform with published physical and spectral data. XeF_2 was prepared by photosynthetic methods [10] and its purity was better than 99,5 %. Methylene chloride was purified [11] and stored over molecular sieves.

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p-Benzoquinone

To a solution of 1,4-dihydroxybenzene (0.11 g, 1 mmol) in methylene chloride (5 ml) XeF_2 (0.169 g, 1 mmol) was added under stirring at 20°C. After a few seconds, the colourless solution turned dark blue and xenon gas was evolved. After 20 min. the reaction mixture was diluted with methylene chloride (15 ml), washed (10 ml of 5 % aqueous $NaHCO_3$) and dried (Na_2SO_4) and the solvent was evaporated in vacuo. The crude product was sublimed to give p-benzoquinone: mp 113°C, yield 0.08 g (74%), mass spectrum m/e 108 (M^+), i.r. spectra is identical with p-benzoquinone.

4-t-butyl-o-benzoquinone

To a solution of 1,2-dihydroxy-4-t-butylbenzene (0.166 g, 1 mmol) in methylene chloride (5 ml) XeF_2 (0.169 g, 1 mmol) was added under stirring at 20°C. After a few seconds the colourless solution turned dark blue and xenon gas was evolved. After 30 min. the reaction mixture was diluted with methylene chloride (15 ml), washed (10 ml of 5% aqueous $NaHCO_3$), dried (Na_2SO_4) and the solvent was evaporated in vacuo. The crude product was purified by t.l.c. to give 0.11 g (67%), mp 69°C (lit. [12] mp 67-70°C), mass spectrum m/e 164 (M^+), n.m.r. ($CDCl_3$) δ 6.25 ppm (d, 1H, H3), δ 6.32 ppm (d, 1H, H6), δ 7.25 ppm (dd, 1H, H5), J (H_3H_5) = 2 Hz, J (H_5H_6) = 10.5 Hz.

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