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UNUSUAL REACTION OF PENTAFLUOROPHENYLMAGNESIUM CHLORIDE

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By the reaction of pentafluorophenylmagnesium chloride (1) with ethylene oxide (2,5:1, in ether, then ether distilled off, benzene was added and mixture was refluxed for 5 hours) we obtained not only normal product - 2-(2,3,4,5,6-pentafluorophenyl)ethanol (2) [yield 25,6%, b.p. 85,5-87°/14 mm., $n^{20}D$ 1,4508 (lit. b.p. 104°/16 mm.), ν_{max} (film) 1503s (aromatic ring), 985s (C-F), 3400 broad (bonded OH), 3630w cm^{-1} (free OH)], but also 2,3,4,5-tetrafluorobiphenyl (1), yield 21%, m.p. 75-76° (subl.), ν_{max}^{KBr} 1503s (aromatic ring), 1015s cm^{-1} (C-F). Found: C, 63,7; H, 2,5; F, 33,2. $C_{12}F_4H_6$ requires: C, 63,7; H, 2,7; F, 33,6. The homogeneity of I was established by gasliquid chromatography and the structure was indicated by its proton NMR spectrum*. This showed singlet at 5 2 p.p.m. (hydrogen in polyfluoroaromatic ring) and a triplet at 6,8

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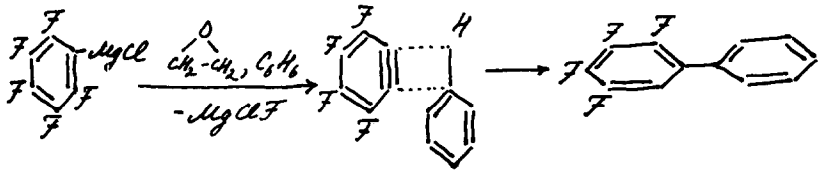
* NMR measurements were carried out at 40 Mc/sec. Chemical shifts are expressed in p.p.m. scale relative to internal tetramethylsilane.

p.p.m. with relative intensity of peaks 2:2:1 phenyl (3); the relative areas have expected ratio 1:5.

The nitration of I with mixture of nitric acid (d 1,52) and glacial acetic acid, then reduction with iron in mixture of water and benzene and finally oxidation by solution of $KMnO_4$ in water led to 2,3,4,5-tetrafluorobenzoic acid [m.p. 79–80° (from C_6H_6), $\nu_{max}^{CCl_4}$ 1715s (C=O in ArCOOH), 1495s and 1505s (aromatic ring), 998m (C–F), 3000 broad (bonded OH in ArCOOH) ; the autentic specimen of this acid was synthesized in our institute by partial decarboxylation of tetrafluorophtalic acid (4).

It must be pointed that if the reaction is finished after refluxing in ether, the ethylene chlorohydrin and pentafluorobenzene (with nearly quantative yield) are the only products, i.e. the Grignard reagent did not react in these conditions with ethylene oxide. Probably when the ether was replaced with benzene and the mixture refluxed in this solvent, the ethylene oxide which was complexed with $MgCl_2$ (5) react with Grignard reagent thus producing not only Mg-alcoholate of β-pentafluorophenylethanol, but also tetrafluorobenzyne. The latter further react with benzene by means of hydrogen abstraction:



Reactions via hydrogen abstraction have been reported for interactions of benzyne with monoolefins and 1,3-cyclohexadien

(6,7). The presence of the intermediate tetrafluorobenzyne was confirmed by isolation of 5,6,7,8-tetrafluoro-1-naphthol [m.p. 121,5-122° (subl.), $\nu_{max}^{CCl_4}$ 3640m (free OH), 1495s (aromatic ring), 1000s (C-F), $\lambda_{max}^{C_2H_5OH}$ 304, 324 and 336 mμ (lg ε 3,54, 3,50 and 3,44) when the reaction was carried in cyclohexane solution of furan inspite of benzene; this naphthol was earlier synthesized from pentafluorophenyllithium and furan (8).

We expected that tetrafluorobenzyne generated from pentafluorophenylmagnesium chloride and ethylene oxide can be employed for introduction of tetrafluorophenyl group in aromatic hydrocarbons and their derivatives. Indeed we have isolated C_6F_4H-$C_6H_4CH_3$ (II) when reaction was carried in toluene, b.p. of II 110-110,5°/11mm., $n_D^{16,5}$ 1,4990, ν_{max}^{KBr} 2999m, 2940m, 2915m and 2860m (CH_3), 1501s (aromatic ring), 1002s cm^{-1} (C-F); UV-spectrum of I and II are very similar.

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