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THE REACTION OF TETRAFLUOROBENZYNE WITH BENZENE

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Tetrafluorobenzyne has been generated in the reaction of pentafluorophenylmagnesium chloride with ethylene oxide in benzene solution.[1] As well as the product from the normal Grignard reaction (2-pentafluorophenyl ethanol), a compound $C_{12}H_6F_4$ was obtained and was assigned the structure 2,3,4,5 - tetrafluorobiphenyl on the basis of elemental analysis and infrared and proton magnetic resonance spectroscopy. However, since the published P.M.R. data do not fit the assigned structure and further since the generation of arynes from o-haloaryl-Grignard and-lithium reagents appears to depend solely on the reaction temperature and not upon the precise nature of the Grignard-ether complex, we have reinvestigated this reaction.

The observation that highly fluorinated aromatic compounds form charge-transfer complexes with electron-rich systems, such as benzene,[2,3] suggests that tetrafluorobenzyne should, in benzene solution, form adducts with benzene and other aromatic systems. This is in contrast to the more typical aryne reaction in which nucleophilic attack by the aryne organometallic precursor occurs.[4,5.] Experiment has now confirmed these arguments.

We have obtained the same aryne products, in approximately the same proportions from pentafluorophenylmagnesium-chloride and-bromide, whether ethylene oxide is present or not. In our experiments we have only detected the presence of small quantities (~5%) of 2-hydrononafluorobiphenyl; identified by gas chromatographic comparison with an authentic sample.[6]

We have not detected the presence of 2,3,4,5-tetrafluorobiphenyl but have instead isolated tetrafluorobenzobicycloocta [2.2.2] triene, in 33% yield, (48% yield from pentafluorophenylmagnesium bromide) bp 100-110°/2.0 m.m., m.p. 70-71° after sublimation or recrystallisation from light petroleum. The structure of this compound is established on the basis of the following evidence.

The infrared spectrum (KBr disc) shows the following bands:- 3085, 3035 (Olefinic C-H stretch), 2940, 2860 (aliphatic C-H stretch), 1638 (Olefinic C=C stretch), 1500 (highly fluoroinated aromatic ring), 1042 (C-F stretch) and 755 cm^{-1}(cis-olefin).

The proton magnetic resonance spectrum shows the presence of multiplets at τ 3.12 (4 protons) and τ 4.72 (2 protons), which collapse to broadened singlets in spin-spin decoupling experiments. It is tentatively suggested that this broadening may be due to long range F^{19}-H coupling.

The F^{19}N.M.R. spectrum shows the presence of two quartets at 8494 c/s (2 fluorines) and at 9200 c/s (2 fluorines) upfield from $CFCl_3$, measured at a frequency of 56.5 M/c.

The ultraviolet spectrum shows only weak absorption in the region 220-400 mμ.

The compound absorbed two moles of hydrogen in the presence of Pd/C to give tetrafluorobenzobicycloocta [2.2.2] ene, m.p. 113-114°.

The I.R. spectrum shows the absence of bands at 3085, 3035, 1635 and 755 cm^{-1} but does show bands at 2970, 2880, 1500 and 1025 cm^{-1}.

The P.M.R. spectrum shows the presence of two multiplets at τ 6.4 (2 protons) and τ 8.35 (8 protons).

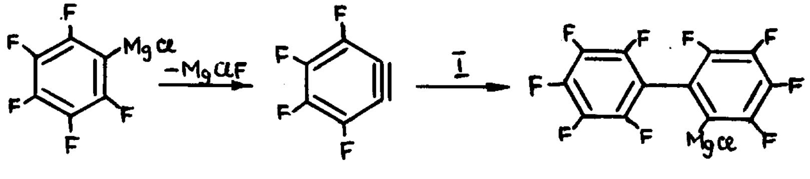
The U.V. spectrum is almost identical to that of the unreduced compound.

Finally, tetrafluorobenzobicycloocta [2.2.2] triene when heated in an evacuated pyrex tube at 325° for 18hr. gave 1,2,3,4-tetrafluoronapthalene, m.p. 106° (lit.[7]m.p. 110-111°) λ_{max} (EtOH), ϵ_{max} and ν_{max}^{KBr}

in good accord with published values.[7]

Since it is well established[1,5,7] that pentafluorophenyl-Grignard- and-lithium reagents easily lose metal fluoride to give tetrafluorobenzyne the formation of our isolated products may be rationalised on the basis of the following series of reactions.

Tetrafluorobenzyne, which is produced from a charge-transfer complex between pentafluorophenylmagnesium chloride and benzene, only reacts to a small extent with the Grignard reagent (I) to give 2-hydrononafluorobiphenyl after hydrolysis.



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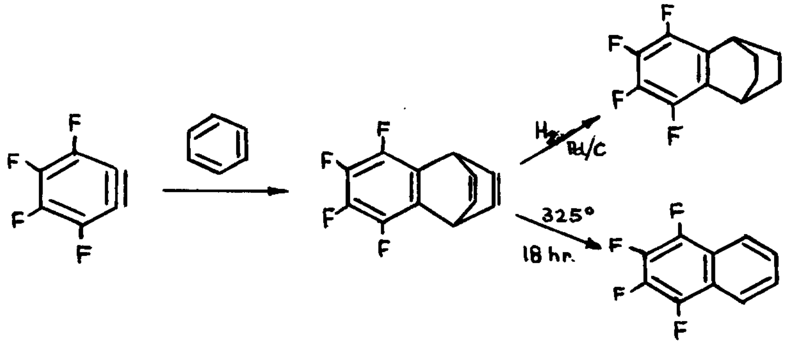
The major reaction occurs between tetrafluorobenzyne and the benzene with which it is associated.



These reactions afford by far the best yields so far obtained of products in which an aryne reacts additively with benzene or other aromatic substrates.

We are at present studying these reactions further with a view to establishing the effect of substituents in the aromatic hydrocarbon on the nature and yields of the products.

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