Formation of 1,2- and 1,4-Cyclo-adducts from Tetrafluorobenzyne and *NN*-Dimethylaniline and a Stevens Rearrangement with Aryl Migration

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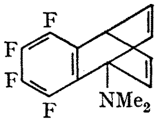
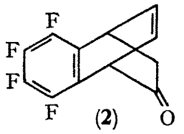
Summary Tetrafluorobenzyne reacts with *NN*-dimethylaniline to give 1,2- and 1,4-cyclo-adducts and solvent dependent products derived from an intermediate betaine.

PRODUCTS derived from intermediate betaines have been obtained in the reactions of benzynes with tertiary amines,[1] including *NN*-dimethylaniline.[2] Tetrahalogenobenzynes react with arenes to form only 1,4-cyclo-adducts,[3] and with thioanisole to yield 2,3,4,5-tetrahalogenophenylthiobenzenes *via* ylides.[4]

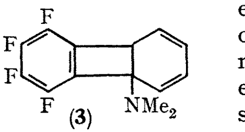
We now report the reactions of tetrafluorobenzyne with *NN*-dimethylaniline. Pentafluorophenylmagnesium chloride reacted at 80° with an excess of *NN*-dimethylaniline to give three products:† (**1**),[3c] (**2**),[3a] and 4a-dimethylamino-5,6,7,8-tetrafluoro-4a,8b-dihydrobiphenylene (**3**) in 10%, 0·75%, and 1·5% yield, respectively.



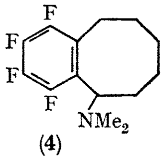
(**1**)



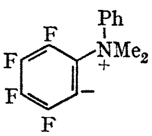
(**2**)



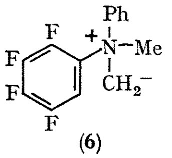
(**3**)



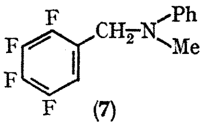
(**4**)



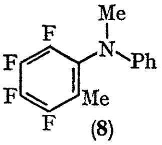
(**5**)



(**6**)



(**7**)



(**8**)

Although the reaction of benzyne with benzene yields, among other products, benzocyclo-octatetraene, the presumed primary product, 4a,8b-dihydrobiphenylene has not been detected.[5] The structure (**3**) provides, as far as we are aware, the first example of this ring system.[6] The u.v. spectrum of (**3**) showed a cyclohexadiene chromophore, λ_{max} 263 nm., ϵ 7000. The ^{1}H n.m.r. spectrum showed resonances at τ 3·38—4·5 (4H), 5·15 (1H), and 7·42 (6H), and structurally significant ions were observed in the mass spectrum at *m/e* 269, 254, 240, 225, and 224. Compound (**3**) gave the expected stable tetrahydro-derivative on catalytic hydrogenation over palladium on carbon. Compound (**3**) was unaffected by brief heating with aqueous mineral acid. Similarly the tetrahydro-derivative was evidently not an enamine from its failure to undergo hydrolysis to a ketone and from its non-reduction with sodium borohydride in methanol. Further catalytic reduction to (**4**) was, however, achieved using Adams catalyst in acetic acid.[7]

Pentafluorophenyl-lithium decomposed in ether containing an excess of *NN*-dimethylaniline to give: (**1**) 5·5%, (**2**) 0·5%, (**3**) 12·5% and a product which was evidently formed by stabilisation of the betaine (**5**). The structure of this product contrasts with those obtained in reactions of benzyne with *NN*-dimethylaniline. Although no verified examples of Stevens rearrangements[8] involving migration of an aryl group have been reported, such a rearrangement might be expected from the ylide (**6**) in view of the strong electron-withdrawing effect of the fluorine atoms. The structure *N*-2,3,4,5-tetrafluorobenzyl-*N*-methylaniline (**7**), isolated in 9·5% yield, was confirmed by the ^{1}H n.m.r. spectrum which showed the aromatic protons as a multiplet at τ 2·68—3·42 and the methylene protons at τ 5·5, and by the mass spectrum in which an ion was present at *m/e* 163 (54·5%) which corresponds to $C_7H_3F_4^+$.

Decomposition of the betaine (**5**) in diethyl ether results therefore from initial charge redistribution. However, in light petroleum five products were obtained: (**1**) 9·5%, (**2**) 10%, (**3**) 2%, (**7**) 0·5%, and (**8**) 19%. Compound (**8**) was shown to be *N*-methyl-*N*-phenyl-tetrafluoro-*o*-toluidine. Thus in this last reaction the major product of stabilisation of the betaine (**5**) was presumably derived by immediate charge neutralisation rather than by formation of the ylide (**6**).

Failure to observe products derived from the betaine (**5**) in the reaction carried out at 80° is probably due to either an unfavourable equilibrium position at this temperature or to stabilisation of the betaine by magnesium halide.

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† Satisfactory analytical data were obtained for all the new compounds reported except (**3**), which rapidly polymerises, but for which accurate mass measurements on the molecular ion and the major fragment ions were obtained by mass spectrometry.

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