

Pentafluoronitrosobenzene as a Source of Aryl Nitrene and  
as a Radical Trapping Agent.

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Received June 26, 1973

Sir:

It has previously been established (1) that electrophilic aryl nitrenes will add to activated aromatic substrates and, if the nitrene is electrophilic enough, e.g., pentafluorophenylnitrene (1), addition even to benzene will take place (2). We now report some unusual products from the reaction of 1 with *N,N*-dimethylaniline and from the trapping of aryl radicals by pentafluoronitrosobenzene (2).

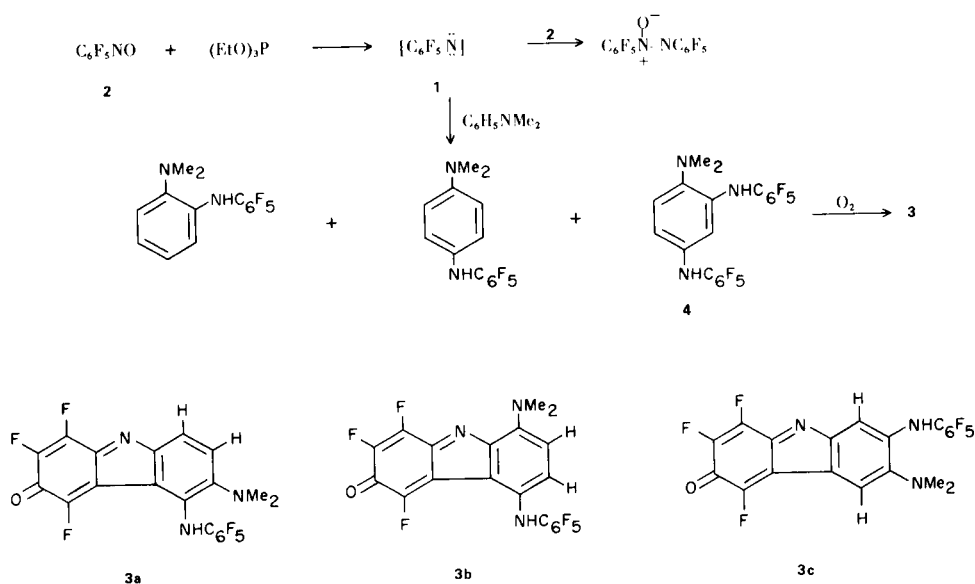
Triethyl phosphite deoxygenation of 2 in an excess of *N,N*-dimethylaniline gave decafluoroazoxybenzene (1.1%), 2'-dimethylamino- (9.4%) and 4'-dimethylaminopentafluorodiphenylamine (4.6%), and a purple solid (3) (10%), M.W. 459, together with traces of a blue compound of undetermined structure. When the reaction was carried out in the absence of air 3 was not formed but instead the disubstitution product 4 (3.7%) was isolated (3) which, on exposure to air, was converted to 3.

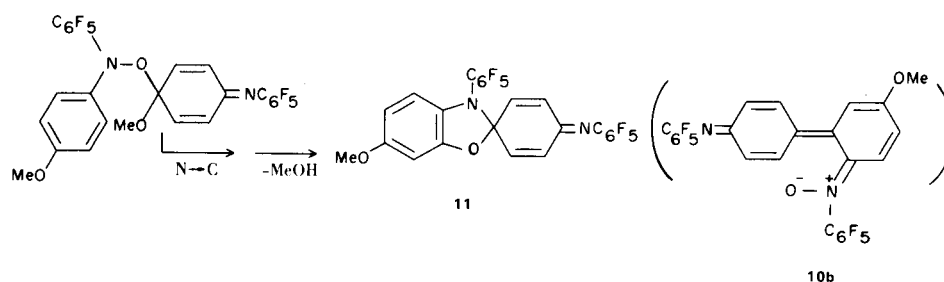
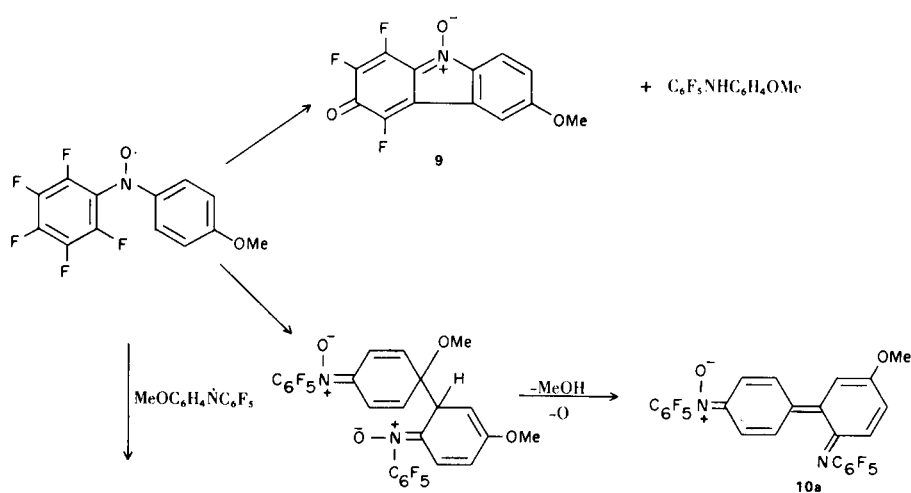
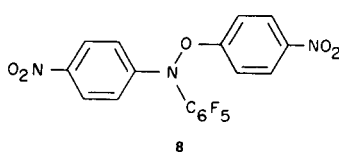
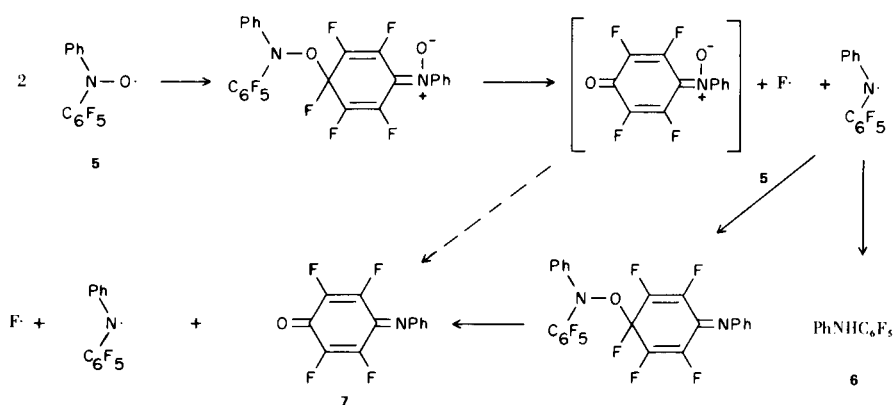
Compound 3 ( $C_{20}H_9F_8N_3O$ ) exhibited bands at 3435 (NH) and 1620  $cm^{-1}$  (C=O), an  $M^+$ -CO peak in the mass spectrum and, in addition to an exchangeable (NH) proton at  $\delta$  5.9 had 1H lines at  $\delta$  7.9 (d,  $J = 9$  Hz) and 7.33 (d,  $J = 9$  Hz). Since 3 is formed from 4, three

carbazolequinone structures are possible (3a-c). The large coupling constant observed eliminates 3c from consideration, while the low field at which one of the protons resonates suggests that it is *peri* to an  $sp^2$  nitrogen (4), so that the purple compound is probably 3a.

The possibility of forming stable nitroxides (5) from 2 and aryl radicals was also investigated. Reaction of 2 with phenyl radicals (from benzenediazonium tetrafluoroborate and choline) in acetonitrile solution gave, on tlc, 5 (4.1%) [red oil;  $m/e$  274 ( $M^+$ ); esr spectrum: triplet  $a_N = 11.0$  gauss, triplet  $a_H = 2.02$  gauss (2 *ortho* H), other  $a = 0.45$  gauss], together with 2,3,4,5,6-pentafluorodiphenylamine (6) (4.3%) (2), and *p*-benzoquinone pentafluoroanil (7) (8.5%), m.p. 78-80°. Compounds 6 and 7 may be viewed as arising from 5 as follows. *p*-Nitrophenyl radicals and 2 gave the nitroxide (4.6%), 2,3,4,5,6-pentafluoro-4'-nitrodiphenylamine (6.5%) and 8 (3%).

The more nucleophilic *p*-methoxyphenyl radicals gave the diphenylamine (1.9%), together with a red solid (2.5%) to which structure 9 has been assigned, and a purple oil (6.2%),  $C_{25}H_{10}F_{10}N_2O_2$ , possibly 10a (the alternative





structure **10b** was eliminated because of the observation of fragment ions at  $m/e$  287 and 273 in the mass spectrum of the purple compound, consistent with cleavage between  $C_1-C_1'$  of the biphenyl group in **10a** but not in **10b**).

Structure **11** is also consistent with the analytical and spectral data but its formation would require  $N \rightarrow C$  oxygen migration followed by loss of methanol.

Carbazolequinone **9** [ $\nu_{C=O}$  1630  $\text{cm}^{-1}$ ;  $\delta$  (chloroform) 6.7-7.1 (br) (3H), 3.95 (s, Me);  $M^+$ ,  $m/e$  281 (100)] may arise from two molecules of the nitroxide (as in the formation of **7**) with cyclization and loss of HF preceding or following radical coupling, which is reminiscent of the conversion of **4** to **3**.

#### Acknowledgments.

This work was supported by a grant from the NSF (GP-33361 X) which is gratefully acknowledged.

#### REFERENCES

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