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THE REACTION OF BENZOFUROXAN WITH P-ANISYLAZIDE: TRAPPING OF THE O-DINITROSO-INTERMEDIATE

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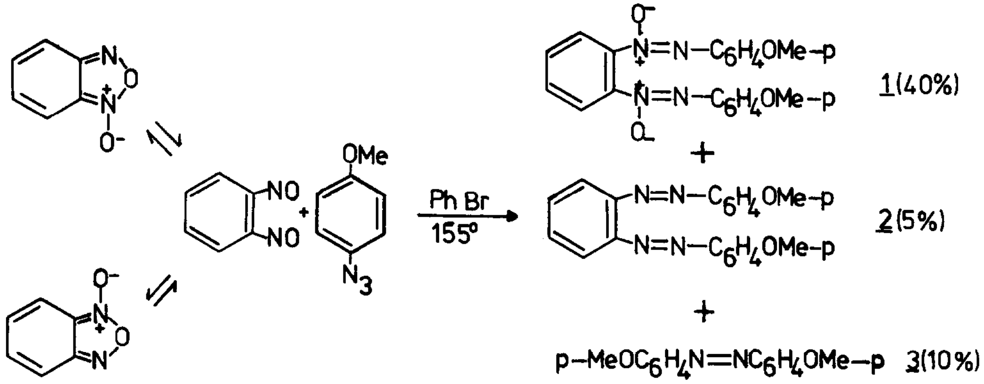
Previous studies using n.m.r. have indicated that benzofuroxan may tautomerise via o-dinitrosobenzene as shown, and the activation energy of this process has been measured[1]. We recently reported the trapping of triplet arylnitrenes by some nitrosoarenes in boiling bromobenzene[2] and thought that we could apply this method to demonstrate chemically the intermediacy of the o-dinitrosocompound.

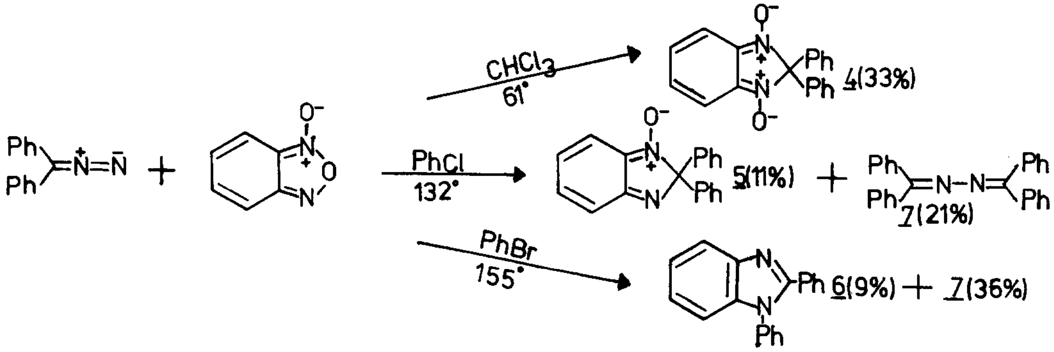
Thermolysis of p-anisylazide (0.02 mole) in bromobenzene, containing benzofuroxan (0.01 mole), at 155° for 8 h yields the products 1, 2, and 3, which are all stable under the reaction conditions. We believe that 1 may arise from the reaction of two molecules of p-anisylnitrene with one molecule of the intermediate o-dinitrosobenzene.



The alternative that p-anisylnitrene may be reacting with benzofuroxan directly rather than with its "tautomer" o-dinitrosobenzene was considered. Since naphtho{1,2-c}furoxan (Ea 20 Kcalmole^{-1})[3] does not tautomerise as readily as benzofuroxan (Ea 15 Kcalmole^{-1})[1], its tautomer 1,2-dinitrosonaphthalene under the same reaction conditions should be less available for trapping than o-dinitrosobenzene. Thermolysis of a mixture of p-anisylazide and naphtho-{1,2-c}furoxan in bromobenzene at 155° gave in fact only naphthofurazan (40%), azoanisole (77%), 2,6-dimethoxyphenazine (4%), and tar. A further argument against the possible formation of 1 directly by attack of nitrene on benzofuroxan is that this type of ring-opening requires a reagent of nucleophilic character[4], a property that has not been reported for arylnitrenes. Moreover, heating p-anisidine with benzofuroxan under the reaction conditions did not give 1 or 2; only intractable tars were obtained.

The structures 1 and 2 were assigned on the evidence of spectral data and elemental analyses, and 1 gave 2 on treatment with triethylphosphite. Support for the intermediacy of a nitrene came from kinetic experiments. This appears to be the first successful trapping of o-dinitrosobenzene, though evidence has recently been advanced for the trapping of certain substituted o-dinitrosobenzenes by acetonylmethyl sulphide[5].

Heating diphenyldiazomethane as a carbene source, with benzofuroxan under a variety of conditions gave no further information about the role of the o-dinitrosointermediate.



The mechanism of formation of 4, 5, and 6 may be similar to that of the reaction between benzofuroxans and substituted nitromethanes[4].

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6. We thank Mr. A.M. Jefferson for help in assigning the structures of 4, 5 and 6.