

A NOVEL REARRANGEMENT: THE RING OPENING
OF A CYCLIC AZO COMPOUND TO A DIAZOALKANE

C. G. Overberger and Jean-Pierre Anselme

Department of Chemistry

Polytechnic Institute of Brooklyn

Brooklyn 1, N.Y.

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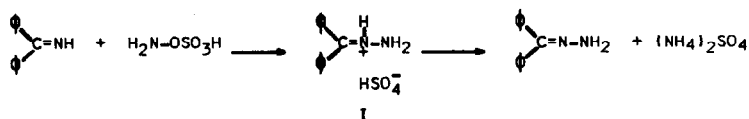
Our general interest in cyclic azo compounds has led us to the study of the three-membered ring azo compounds¹, also called diazirines or 1-diazacyclopropenes. In the course of the attempted synthesis of diphenyl-1-diazacyclopropene(III), an unusual rearrangement was discovered. The reaction of benzophenone imine hydrochloride in liquid ammonia at -70° with a methanolic solution of hydroxylamine-O-sulfonic acid gave a white reaction mixture which after standing for a day in contact with air, turned deep red. When the reaction mixture was worked up immediately, no red color developed. However, after standing two days in air, the same change to red occurred again. No red coloration was observed when the reaction was carried out under nitrogen. However, the introduction of oxygen or the

(1) S.R.Paulsen, Angew.Chem., 72, 781 (1960); E.Schmitz and R.Ohme, Chem. Ber., 94, 2166 (1961); 95, 795 (1962).

addition of mercuric oxide caused the red color to appear. Diphenyldiazomethane(IV) was identified from the red solutions by its conversion to benzophenone azine(VI) and by comparison of its infrared spectrum with that of an authentic sample.

The possibility that benzophenone oxime O-sulfonic acid was being formed by the reaction of the imine with hydroxylamine-O-sulfonic acid, then undergoing a Forster reaction² was excluded on the basis that no diphenyldiazomethane was formed in the absence of oxidizing agents (air, mercuric oxide). The generation of diazoalkanes begins with the addition of the reagents in the Forster reaction.

The other alternative that diphenyldiazomethane arose via a Forster-type reaction of the imine was discounted on mechanistic grounds. Indeed the addition of hydroxylamine-O-sulfonic acid to the imine would yield the salt of benzophenone hydrazone(I). The chances of its existence in the presence of excess base are, at best, remote.



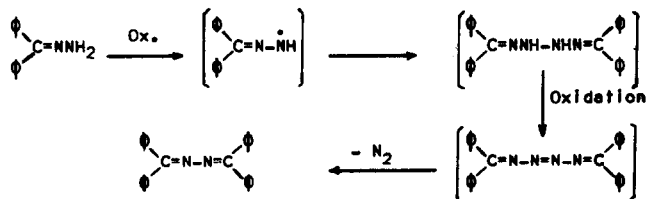
The conversion of the salt of the hydrazone(I) to diphenyldiazomethane with base by a mechanism similar to that of the Forster reaction would involve a hydride transfer, a very unlikely process in liquid ammonia. Under certain conditions, benzophenone hydrazone can be oxidized to diphenyldiazomethane^{3,4} which then slowly decomposes to benzophenone azine. It is

(2) M.O. Forster, *J. Chem. Soc.*, 107, 260 (1915); J. Meinwald, P.G. Gassman and E.G. Miller, *J. Am. Chem. Soc.*, 81, 4757 (1959).

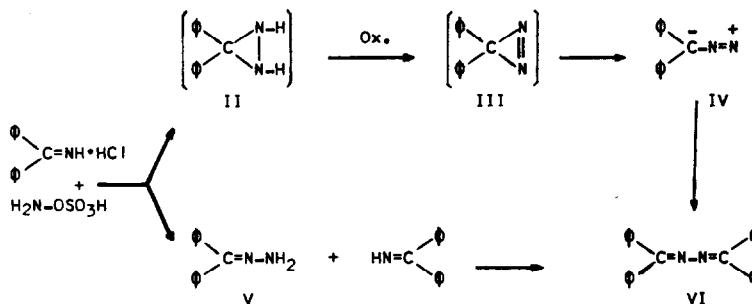
(3) H. Staudinger and O. Kupfer, *Ber.*, 44, 2197 (1911).

(4) D.H.R. Barton, R.E. O'Brien and S. Sternhell, *J. Chem. Soc.*, 470 (1962).

known that the free radical oxidation of benzophenone hydrazone to the azine does not involve diphenyldiazomethane as an intermediate^{4,5}; a hypothetical and unstable tetrazone is thought to be the intermediate.



Therefore a new kind of rearrangement must be involved, namely the ring opening of the cyclic azo compound to its open chain isomer (III \rightarrow IV). We have checked the possibility that benzophenone hydrazone was being oxidized to diphenyldiazomethane under the conditions of our reaction. No trace of diphenyldiazomethane was found. The presence of a three-membered ring azo compound (III) as an intermediate thus became the only logical explanation for the formation of diphenyldiazomethane. The scheme below outlines the different pathways which can lead to diphenyldiazomethane and benzophenone azine.



(5) M.Z. Barakat, M.F.A. El-Wahab and M.M. El-Sadr, J. Am. Chem. Soc., **77**, 1670 (1955).

It is possible for hydroxylamine-O-sulfonic acid to lose the elements of sulfuric acid to give the so-called "nitrene"(N-H) which then adds across the $C=N$ - bond of the imine to form the three-membered ring hydrazine(III). It can also add in the normal manner to give the hydrazone(V). Air oxidation or more likely reaction with benzophenone imine would convert the hydrazone to the azine(VI). Air oxidation of the three-membered ring hydrazine(III) can then give the azo compound(III). The driving force for this rearrangement is provided by the presence of the two bulky phenyl groups which would increase the strain in the three-membered ring azo compound. Furthermore diphenyldiazomethane is fairly stable and linear. This may explain the facile ring opening of the azo compound⁶. All attempts to isolate the three-membered ring azo compound(III) failed.

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(6) W.H.Graham has found that the reaction of fluorenone imine with difluoroamine, J. Am. Chem. Soc., **84**, 1063(1962), does not give the expected diazirine. Instead, diazofluorene is isolated. This is analogous to our findings. We wish to thank Dr. Graham for communicating his results to us.