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^{15}N STUDY OF THE PHENYLDIAZENYL RADICAL: A SEARCH FOR PHENYL MIGRATION

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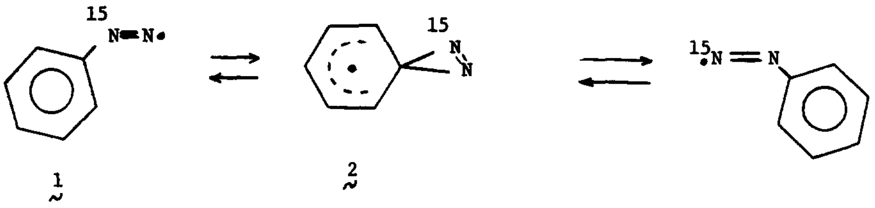
The phenyldiazenyl radical Ph-N_2•, 1, has been established as an intermediate in the decomposition of several unsymmetric azo compounds. Stereochemical studies[1], solvent viscosity effects[2], deuterium isotope effects[3], and most recently CIDNP evidence[4] all support the intermediacy of PhN_2• . Little experimental evidence concerning the structure of PhN_2• has been presented, however. CIDNP studies[4] suggest that it is a σ radical and calculations support this view indicating a bent structure with a C-N-N angle of about 135°.[5] The known propensity for phenyl migration in β phenethyl radicals[6] suggests that the degenerate rearrangement of 1 (Scheme I) is possible. A spirodiazirine cation analogous to 2 has, in fact, been proposed as an intermediate in the decomposition of benezendiazonium salts.[7,8] Lewis and Insole[7] observed 2% exchange of α and β nitrogen during decomposition of the salt to 80% completion and Swain, Sheats, and Harbison[8] have recently confirmed this earlier observation.

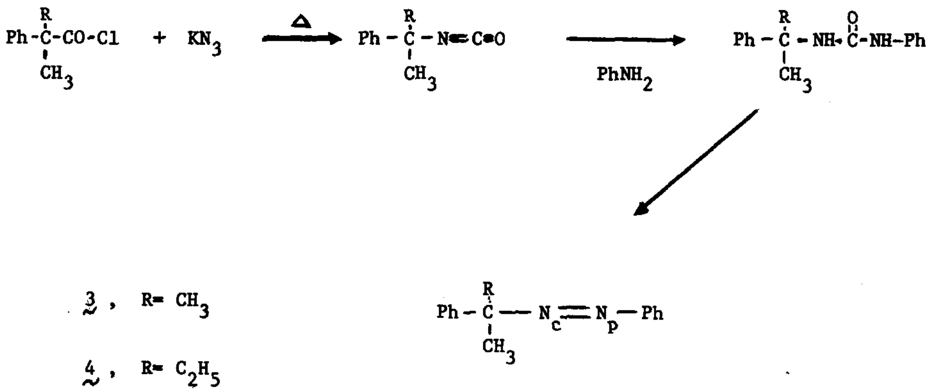


Scheme I

We report here results which show no detectable scrambling of a nitrogen label in the phenyldiazenyl radical, 1. The lack of rearrangement observed in the diazenyl radical is in marked contrast to β-phenethyl radical systems where rearrangement approaches100% in some cases.[6]

The system chosen for study was the azo compound 3. The synthetic approach is a modification of the reported synthesis of 3.[1b] The Curtius method used here, however, conveniently introduces label at either nitrogen. Thus, 3 with the nitrogen attached to the phenyl group (N_p) labelled with 97% ^{15}N could be prepared from labelled aniline. The cumyl nitrogen (N_c) could be labelled to the extent of 50% from ^{15}N potassium azide.

Scheme II



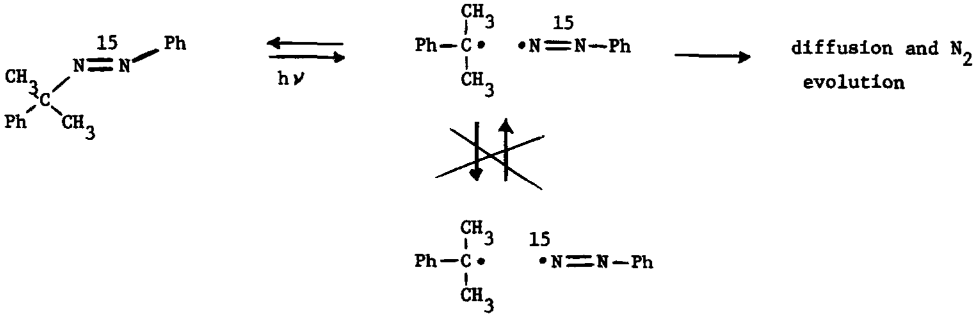
^{15}N magnetic resonance spectra of the labelled azo compounds were obtained on a Bruker HFX 10 spectrometer. The signal due to the phenyl nitrogen (N_p) is found 132 ppm downfield from $^{15}NO_3^-$.[9] Absorption due to N_c is found 170 ppm downfield from $^{15}NO_3^-$.

The azo compound labelled at N_p (97%) was photolyzed in benzene with pyrex filtered light from a 450 watt medium pressure Hg lamp until 50% of the compound remained. An analogous optically active azo compound **4**, when photolyzed under comparable conditions was previously reported to show considerable racemization at the carbon α to the azo linkage.[1a] This experiment, along with CIDNP experiments reported previously[4] demonstrate that under these conditions the phenyldiazenyl radical is formed and undergoes internal return to the starting azo compound.

Labelled azo compound remaining after photolysis as described (vide supra) was isolated from the photolysate and purified by HPLC.[10] Recovered **3** obtained in this way showed only the ^{15}N absorption due to N_p label after 55,000 scans. Signal to noise for the N_p signal was greater than 320/1. We would thus have been able to detect at least 0.6% label at N_c if present.

We conclude that rearrangement of the phenyldiazenyl radical in this system is indetectably small. (Scheme III). ^{15}N CIDNP studies to be published also indicate no detectable rearrangement.

Scheme III



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(9) The ^{15}N standard was 5.8 M $^{15}NH_4\,^{15}NO_3$ in 2 M HNO_3.

(10) Liquid chromatography was on 8' of Porasil A, 0.2% Ether in hexane solvent using a Waters ALC 202.