

EVIDENCE FOR THE INTERMOLECULAR MECHANISM IN THE PHOTOISOMERIZATION OF
N-NITROSODIALKYLAMINES TO AMIDOXIMES

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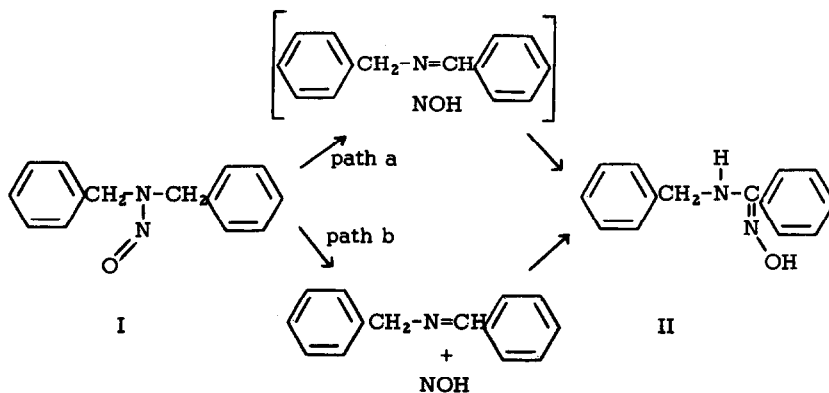
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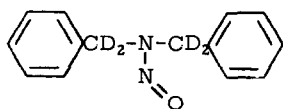
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Simple N-nitrosodialkylamines were first shown in 1964 to undergo a facile isomerization to the corresponding amidoximes when irradiated in the presence of a proton donor (1, 2). For example, N-nitrosodibenzylamine (I) is converted to its photoisomer, N-benzylbenzamidoxime (II), in 90% yield. Recent reports by Chow (3), and Adam and Schreiber (4) describe the scope of this reaction and illustrate some of the synthetic applications.

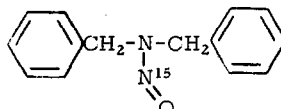
While the over-all course of this reaction seems to be fairly well described, some of the mechanistic features remain obscure. Since Chow has obtained evidence for the presence of both nitroxyl and alkylideneimine as reaction intermediates it is reasonable to consider two mechanistic pathways for this photoisomerization. One pathway is an intramolecular process involving the elimination of nitroxyl to form an alkylideneimine, followed by recombination of these species within the original solvent cage (path a). The other pathway is an intermolecular process in which the generated species diffuse from the original solvent cage and random combination follows (path b).



To distinguish between these possibilities, an equimolar mixture of $\alpha, \alpha', \alpha'', \alpha'''$ -tetra-deutero-N-nitrosodibenzylamine (III) and N-[N¹⁵-nitroso]-dibenzylamine (IV) in methanol-



III



IV

water (6:1) containing an equivalent of HCl was irradiated for 16 hrs in a pyrex flask.¹ The data obtained from the mass measurement of the molecular ions of the resulting N-benzylbenzamidoximes are summarized in Table I.

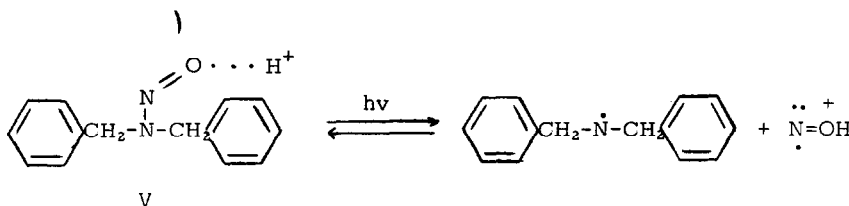
TABLE I

Mass Measurement of Amidoxime Molecular Ions Obtained from Crossover Experiment

Calcd. Mass	Formula	Found Mass	Rel. Abundance ^a
226.111	C ₁₄ H ₁₄ N ¹⁴ N ¹⁴ O	226.111	0.96
227.107	C ₁₄ H ₁₄ N ¹⁴ N ¹⁵ O	227.108	1.00
228.124	C ₁₄ H ₁₂ D ₂ N ¹⁴ O	228.123	0.93
229.120	C ₁₄ H ₁₂ D ₂ N ¹⁴ N ¹⁵ O	229.122	0.90

^a Relative to C₁₄H₁₄N¹⁴N¹⁵O

The possibility arises that the isotope exchange may result from the dissociation-recombination of the photo-excited nitrosamine-proton complex (V). That this process

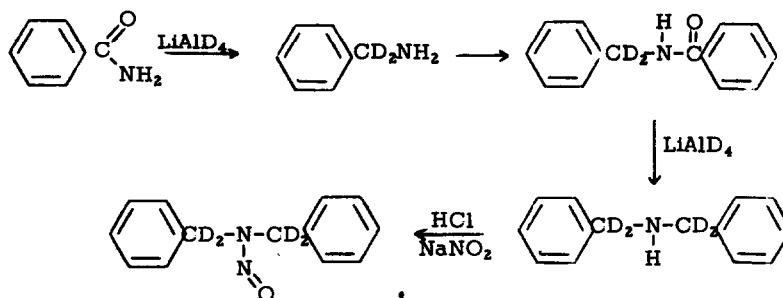


does occur is consistent with the quantum yields ($\Phi = 0.75$) observed by Burgess and Lavanish (1). When the reaction mixture from the photolysis of an equimolar mixture of

¹ A Southern New England Ultraviolet Co. chamber reactor, model RPR-100, equipped with 3500 Å lamps operating at 35°C was used.

Compounds III and IV was analyzed after 45% conversion to the amidoximes, the mass spectrum showed the absence of a molecular ion corresponding to $C_{14}H_{10}D_4N^{14}N^{15}O$ (m/e , 231.133). This observation indicates that to the extent that this geminate recombination takes place it must occur wholly within the original solvent cage and thereby not contribute to the observed isotope crossover. Similarly, the labeled *N*-benzylbenzamidoximes were shown not to undergo isotope exchange under the reaction conditions. From the extensive crossover of the isotopes that takes place on irradiation it is possible to conclude that the nitrosoamine-amidoxime photo-isomerization is largely an intermolecular process (path b).

The synthesis of the $\alpha,\alpha,\alpha',\alpha'$ -tetradeutero-*N*-nitrosodibenzylamine was accomplished by the following route:



Compound IV was prepared by nitrosation of dibenzylamine using HCl and $NaN^{15}O_2$. Mass spectrometry indicated compounds III and IV to be a minimum of 97% $C_{14}H_{10}D_4N_2^{14}O$ and $C_{14}H_{14}N^{14}N^{15}O$, respectively.

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References

- (1) E. M. Burgess and J. M. Lavanish, *Tetrahedron Letters*, 20, 1221 (1964).
- (2) Y. L. Chow, *Tetrahedron Letters*, 34, 2333 (1964).
- (3) Y. L. Chow, *Can. J. Chem.*, 45, 53 (1967).
- (4) G. Adam and K. Schreiber, *Tetrahedron*, 22, 3591 (1966).