

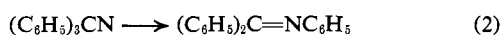
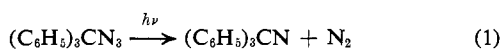
# Carbon–Nitrogen Cleavage in the Photolysis and Pyrolysis of Triphenylmethyl Azide<sup>1</sup>

Frederick D. Lewis and William H. Saunders, Jr.

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. Received January 24, 1968

**Abstract:** The formation of triphenylmethyl radical in the photolysis of triphenylmethyl azide is demonstrated by its esr spectrum. Photolysis of azide labeled in the terminal nitrogen with nitrogen-15 leads to isotope-position rearrangement, suggesting that recombination of triphenylmethyl and azide radicals occurs. Pyrolysis of the labeled azide results in extensive isotope-position rearrangement. No radicals can be detected in the pyrolysis products by esr measurement, however, so the rearrangement probably occurs by an intramolecular process or ion-pair recombination.

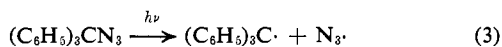
We have previously studied the direct<sup>2</sup> and sensitized<sup>3</sup> photolyses of triarylmethyl azides. Only products corresponding to loss of nitrogen followed (or accompanied) by rearrangement to a benzophenone phenylimine (eq 1 and 2) were observed.



Initial efforts to determine the quantum yield led to values near 0.01, in sharp contrast to the high quantum yields for ethyl azide<sup>4</sup> (1.0) and other simple alkyl azides<sup>5</sup> (0.7–0.9). Further investigation disclosed that the quantum yield was near 0.8 for the first few per cent reaction but decreased rapidly with increasing conversion due to the formation of a yellow substance which absorbs much more strongly than the expected benzophenone phenylimine at the wavelength of the photolysis and which functioned as an effective internal filter.

A likely candidate for such intense absorption at low concentrations was the triphenylmethyl radical. Consequently, a solution of the azide in benzene was degassed, photolyzed, and allowed to stand in the dark for a time so that no transient radicals would complicate the experiment. The esr spectrum of the solution was identical with that of an authentic sample of triphenylmethyl radicals.<sup>6</sup> A control experiment showed that the radical spectrum could not have come from the only likely impurity, triphenylcarbinol.

These results show that a second primary process, eq 3, is occurring to some extent in the photolysis, though the sensitivity of the esr measurements is so high that



its contribution could be very minor. In order to assess its importance and to determine the fate of the azide radicals, we undertook tracer experiments.

Triphenylmethyl azide labeled with <sup>15</sup>N in the terminal ( $\gamma$ ) nitrogen was prepared by treatment of tri-

phenylmethylhydrazine hydrochloride with sodium nitrite-<sup>15</sup>N in glacial acetic acid. Reduction of the product with lithium aluminum hydride in ether yielded triphenylmethylamine with 1.5% of the <sup>15</sup>N label. We assume, in subsequent calculations of isotope-position rearrangement, that the  $\alpha$ -nitrogen of the original azide was labeled to this extent, though it is possible that shuffling of the label accompanied the reduction. Thus, the percentages of retention of label quoted in Table I are maximum figures which could be as much as 1.5% lower.

When the labeled azide was photolyzed and the evolved nitrogen examined in the mass spectrometer, an average of 10.7% of the label was found to have rearranged away from the  $\gamma$ -nitrogen. If the mechanism of this process is recombination of triphenylmethyl and azide radicals after rotation with respect to each other, then 21.4% of the photolysis could have proceeded *via* eq 3. This mechanism involves the formation of no stable products other than benzophenone phenylimine, and none has been isolated in our work. Benzophenone phenylimine plus unreacted azide account for 93% of starting material. The imine alone accounts for 83% of unrecovered azide, the only other product being an amorphous solid amounting to only 0.2% of the starting material.<sup>2</sup> It seems unlikely that products from trityl radical in yields of 15–20% would have been missed. Finally, recombination provides an attractive explanation of the quantum yield of 0.8. It is, within experimental error, just the value expected from the 21.4% of dissociation–recombination calculated for this mechanism.

Apparent shuffling of the label could also arise from a unimolecular or bimolecular decomposition of azide radical. The former is unlikely, for decomposition of the ground state of the azide radical into a nitrogen molecule plus a nitrogen atom is allowed by correlation rules only when excited products result, and is then endothermic by 62 kcal/mol.<sup>7</sup> A bimolecular reaction of two azide radicals can be excluded by our mass spectrometric data, for it would produce doubly labeled nitrogen molecules 25% of the time (assuming statistical end-to-end combination). In fact, the proportion of doubly labeled nitrogen molecules is within experimental error of that calculated assuming natural abun-

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) W. H. Saunders, Jr., and E. A. Caress, *J. Am. Chem. Soc.*, **86**, 861 (1964).

(3) F. D. Lewis and W. H. Saunders, Jr., *ibid.*, **89**, 645 (1967).

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(5) F. D. Lewis, unpublished results.

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**Table I.** Determination of Nitrogen-15 from Triphenylmethyl Azide-<sup>15</sup>N

Source of nitrogen	Reaction	Time	% m/e 29	
			Obsd <sup>a</sup>	Cor <sup>b</sup>
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CNH <sub>2</sub> <sup>c</sup>	Kjeldahl, then NaOBr		3.79	3.07
			3.67	2.95
		Av	3.73	3.01
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CN <sub>3</sub>	<i>hν</i> , C <sub>6</sub> H <sub>14</sub>	90 min	86.7	87.8
		90 min	88.7	89.8
		90 min	89.2	90.3
		Av	88.2	89.3
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CH <sub>3</sub>	Pyrolysis, C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	3 hr, 150°	65.1	64.2
		12 hr, 150°	54.4	54.8
		2 hr, 190°	54.5	55.0
		2 hr, 190°	53.4	53.8
		Av <sup>d</sup>	54.1	54.5

<sup>a</sup> Determined with an Atlas CH-4 mass spectrometer at 70 eV and corrected for background only. <sup>b</sup> Corrected for the natural abundance of <sup>15</sup>N in N<sub>2</sub> (2 × 0.36%) and (for nitrogen from photolysis and pyrolysis of the azide) for 1.5% of isotope-position rearrangement away from the  $\gamma$ -nitrogen atom in the starting azide. (The 3.0% observed <sup>15</sup>N in N<sub>2</sub> from the  $\alpha$  position must be divided by a statistical factor of 2, since both nitrogens of the N<sub>2</sub> come from the  $\alpha$  position.) <sup>c</sup> Obtained by reduction of starting triphenylmethyl azide with lithium aluminum hydride in ether. <sup>d</sup> Average of last three numbers only.

dance of <sup>15</sup>N in the  $\beta$ -nitrogen (see Experimental Section).

We conclude that the most reasonable explanation of our results is a light-induced dissociation into radicals (eq 3) to the extent of 15–20% of the total primary processes, followed predominantly by radical recombination to triphenylmethyl azide with rearranged label. Given the sensitivity of the esr measurements, we cannot exclude the possibility that radical production is an insignificant side reaction accompanying a predominantly intramolecular rearrangement of label, but we prefer the simpler hypothesis that the two phenomena have a common origin.

Pyrolysis of the labeled triphenylmethyl azide was originally intended to demonstrate the location of the label, and we noted with some surprise that the label was in fact much more rearranged than in the photolysis (Table I). An obvious explanation would be a thermal radical dissociation followed by recombination just as in the photochemical reaction, but we were unable to detect radicals by esr in a sample of triphenylmethyl azide which was heated for 30 min at 170° and then cooled rapidly. Of course radicals may have formed and not survived under the reaction conditions. The high nitrogen yield (95%) and our previous inability to isolate any products derived from triphenylmethyl radical<sup>8</sup> argue against this interpretation, though not conclusively.

Alternate hypotheses include a strictly intramolecular isotope-position rearrangement, or dissociation into an ion pair (triphenylmethyl cation and azide anion) which then recombine. A study of the effect of solvent polarity on rate of isotope-position rearrangement could test the ion-pair mechanism.

## Experimental Section

**Triphenylmethylhydrazine hydrochloride** was prepared by the method of Weygand and Steglich.<sup>9</sup>

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(9) F. Weygand and W. Steglich, *Chem. Ber.*, **92**, 313 (1959).

**Triphenylmethyl Azide-<sup>15</sup>N.** To a stirred suspension of 2.0 g (0.0064 mol) of triphenylmethylhydrazine hydrochloride in 60 ml of glacial acetic acid under dry nitrogen was added 0.4 g (0.0044 mol) of sodium nitrite-<sup>15</sup>N (99.5% <sup>15</sup>N, Isomet Corp.) over a 30-min period at room temperature. Ether was added and the mixture extracted with saturated sodium bicarbonate to remove acetic acid. The ether solution was dried and evaporated and the residue taken up in hexane and chromatographed on grade II neutral alumina. The first component eluted was essentially pure triphenylmethyl azide-<sup>15</sup>N in 47% yield (0.60 g, mp 60–62°). A mixture melting point with authentic unlabeled azide<sup>9</sup> was undepressed.

**Reduction of triphenylmethyl azide-<sup>15</sup>N** was performed by the method of Boyer.<sup>10</sup> A solution of 0.108 g (0.0038 mol) of triphenylmethyl azide-<sup>15</sup>N in 10 ml of dry ether was added to a suspension of 0.11 g (0.0028 mol) of lithium aluminum hydride in 20 ml of dry ether. The mixture was refluxed for 5 hr, water added cautiously, and the solution filtered. The ether solution was dried and the ether removed to yield 0.092 g (4%) of triphenylmethylamine, melting point and mixture melting point with an unlabeled sample 93–94°.

**Conversion of Triphenylmethylamine to Nitrogen.** A standard Kjeldahl procedure<sup>11</sup> was used to convert about 10<sup>-4</sup> mol of triphenylmethylamine to ammonia in essentially quantitative yield. The ammonia solution was made slightly acidic with dilute sulfuric acid and concentrated to about 5 ml. This solution was placed in one arm of a two-arm Pyrex apparatus fitted with a break-seal side tube. Into the other arm was placed an excess of 0.5 M potassium hypobromite solution.<sup>12</sup> The apparatus was degassed by four freeze–pump–thaw cycles and sealed under high vacuum. The contents were warmed and mixed. After nitrogen evolution ceased, the contents were again frozen and the break-seal side tube connected to an evacuated mass spectrometer sample tube *via* an evacuated adapter containing powdered Drierite. The break-seal was broken to expand the nitrogen into the sample tube.

**Photolysis of Labeled Triphenylmethyl Azide.** A solution of 0.030 g of the azide in 10 ml of spectro grade hexane in a Vycor tube with a break-seal side arm was degassed by four freeze–pump–thaw cycles and sealed under high vacuum. It was then irradiated for 90 min with a Hanovia 679A medium-pressure mercury lamp. The evolved nitrogen was transferred to a mass spectrometer sample tube as described above.

**Pyrolysis of Labeled Triphenylmethyl Azide.** A solution of 0.020 g of labeled azide in 10 ml of nitrobenzene in a Pyrex tube with a break-seal side arm was degassed by four freeze–pump–thaw cycles and sealed under vacuum. The tube was then heated for the specified time in an oil bath controlled to within  $\pm 0.5^\circ$  of the specified temperature (Table I). The evolved nitrogen was transferred to a mass spectrometer sample tube as described above.

**Esr Study of Photolysis Product.** A 0.1 M solution of triphenylmethyl azide in purified benzene in a Pyrex tube was degassed and sealed as above. It was then irradiated with a Hanovia 679A medium-pressure mercury lamp for 2 hr. The tube was left in the dark for more than 1 hr to allow for the disappearance of transient radicals and the esr spectrum then determined on a JEOLCO 3BSX esr spectrometer with 100-kc field modulation. The spectrum was the same as that of a known sample of triphenylmethyl radical prepared by the method of Lewis.<sup>13</sup>

**Control Experiment.** Since other triphenylmethyl derivatives have been reported to photolyze to triphenylmethyl radical,<sup>14,15</sup> we tested the possibility that the observed spectrum could have come from triphenylcarbinol, the precursor of the azide and a likely impurity. The absence of a hydroxyl stretching frequency in the ir limits the triphenylcarbinol content of our sample to *ca.* 1%. A 0.001 M solution of triphenylcarbinol in purified benzene was photolyzed in the same manner as the azide solution. No esr signal could be detected.

**Esr Study of Pyrolysis Product.** A 0.04 M solution of triphenylmethyl azide in di-*n*-butyl Carbitol in a Pyrex tube was degassed by six freeze–pump–thaw cycles and sealed. It was heated for 30 min at 170° and then cooled rapidly. An attempt to determine the

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(11) D. F. Hillenbrand, Jr., and C. A. Pentz, "Organic Analysis," Vol. 3, Interscience Publishers, Inc., New York, N. Y., 1956, p 136.

(12) K. Clusius and H. H. Buhler, *Helv. Chim. Acta*, **37**, 2361 (1954).

(13) G. N. Lewis, D. Lipkin, and T. T. Magel, *J. Am. Chem. Soc.*, **66**, 1575 (1944).

(14) H. G. Lewis and E. D. Owen, *Chem. Commun.*, 216 (1966); *J. Chem. Soc.*, **B**, 422 (1967).

(15) Y. J. Kozlov and D. N. Shigorin, *Dokl. Akad. Nauk SSSR*, **161**, 871 (1965).

esr spectrum in the same manner as for the photolysis product resulted in no detectable signal.

**Determination of Isotopic Composition.** Mass spectra were determined on an Atlas CH-4 instrument at an ionizing voltage of 70 eV. The background was scanned before each run. The  $m/e$  28 peak in the background was usually 2–4% that in the sample. Background was subtracted from the  $m/e$  28 and 29 peaks before computing the per cent  $^{29}\text{N}_2$ . This percentage was then corrected for the natural abundance of  $^{29}\text{N}_2$  ( $2 \times 0.36\%$ ) and for 98.0%  $^{15}\text{N}$  in the terminal nitrogen of the reactant triphenylphenyl azide in order to calculate the per cent retention of label. The results are

recorded in Table I. The peak at  $m/e$  30 was scanned for the nitrogen from two of the photolyses and found to be  $0.41 \pm 0.01\%$  of the peak at  $m/e$  29. Assuming natural abundance of  $^{15}\text{N}$  in the next-to-terminal nitrogen of the triphenylmethyl azide and neglecting isotope effects, this figure should be approximately 0.36%. Similarly, nitrogen from three of the pyrolyses gave a peak at  $m/e$  30 which was  $0.35 \pm 0.02\%$  of the peak at  $m/e$  29.

**Acknowledgment.** We wish to thank Professor R. W. Kreilick for advice and assistance on the esr measurements.

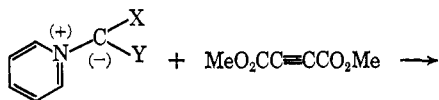
## Syntheses of Fused Aromatic Heterocycles by 1,3-Dipolar Addition Reactions. 1,3a-Diazapentalenes<sup>1</sup>

V. Boekelheide<sup>2</sup> and N. A. Fedoruk

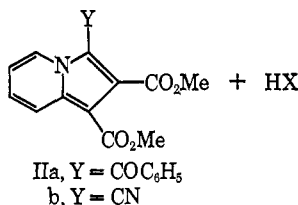
Contribution from the Department of Chemistry,  
University of Oregon, Eugene, Oregon 97403. Received January 2, 1968.

**Abstract:** The reaction of acetylenic esters with ylides derived from imidazole yields derivatives of 1,3a-diazapentalene (IV). The properties of this new class of compounds indicate the presence of aromatic character and are analogous to those of the known 3a,6a-diazapentalenes (III). Unexpectedly, the dicyanomethyl ylides of imidazole and thiazole underwent addition with dimethyl acetylenedicarboxylate to give derivatives of pyrrocoline rather than pentalene.

The reaction of pyrrocoline with dimethyl acetylenedicarboxylate to form cycl[3.2.2]azine derivatives was first observed in 1959.<sup>3</sup> Subsequently, it was shown that this type of 1,3-dipolar addition reaction to give fused aromatic heterocycles is general in nature and can be employed with various heterocyclic zwitterions.<sup>4–7</sup> However, thus far, all of the examples studied have involved the reaction of six-membered heterocyclic zwitterions such as I, yielding substituted pyrrocolines such as II.



Ia, X = H; Y = C(=O)C<sub>6</sub>H<sub>5</sub>  
b, X = Y = CN



IIa, Y = COC<sub>6</sub>H<sub>5</sub>  
b, Y = CN

In view of the current interest in azapentalenes as examples of Hückel aromatic systems,<sup>8,9</sup> it seemed desirable to investigate whether this type of 1,3-dipolar addition reaction might be applied to five-membered heterocycles to give appropriately substituted azapentalenes. This goal has now been realized and the present report describes the synthesis of certain 1,3a-diazapentalene derivatives.

The dianion of pentalene has been prepared by Katz, Rosenberger, and O'Hara, and its properties<sup>10</sup> are in accord with the Hückel molecular orbital picture, as summarized in Figure 1, in which the highest occupied orbital is nonbonding. Intuitively, it would be expected that, if two of the carbons in the pentalene dianion were replaced by pyrrole-type nitrogen atoms, the resulting molecule, aside from being neutral rather than ionic, would have rather similar properties. As shown in Figure 1, placing the two nitrogen atoms at bridgehead positions as in 3a,6a-diazapentalene (III)<sup>11</sup> leads to the HMO prediction that, although there is some displacement of bonding levels to lower energies, the highest occupied orbital is still essentially a nonbonding orbital.<sup>12</sup> Again, the properties of 3a,6a-diazapentalene (III), as described by Solomons and Trofimenko,<sup>8</sup> are in accord with the molecular orbital

(1) Supported in part by the National Heart Institute of the National Institutes of Health, Grant HE-09813.

(2) Roche Anniversary Fund Fellow. We thank the Roche Fund for partial support of this investigation.

(3) (a) A. Galbraith, T. Small, and V. Boekelheide, *J. Org. Chem.*, **24**, 582 (1959); (b) A. Gailbraith, T. Small, R. A. Barnes, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 453 (1961).

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(6) R. Huisgen, R. Grashey, and E. Steingruber, *Tetrahedron Letters*, 1441 (1963).

(7) V. Boekelheide and N. A. Fedoruk, *J. Org. Chem.*, **32**, 2062 (1967).

(8) With regard to 3a,6a-diazapentalene, see (a) T. W. G. Solomons and C. F. Voight, *J. Am. Chem. Soc.*, **88**, 1992 (1966), and (b) S. Trofimenko, *ibid.*, **88**, 5588 (1966).

(9) For a discussion of the dibenzotetraazapentalenes and related compounds, see R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, *ibid.*, **89**, 2618 (1967), and the accompanying papers in their series on aromatic azapentalenes.

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(11) The numbering system which we are employing follows that recommended by Carboni, *et al.*<sup>9</sup>

(12) We are very much indebted to Dr. C. E. Klopfenstein for the use of his computer program and his assistance in making these calculations.