

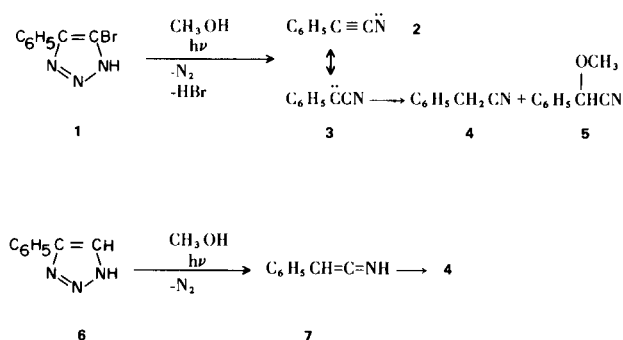
Photo-elimination of Nitrogen from Fused-ring Triazoles (1)

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By irradiation in methanol at 3000Å, aniline and *o*-anisidine were produced from benzotriazole and *N*-methylaniline and *N*-methyl-*o*-anisidine were produced from *N*-methylbenzotriazole. Carbazole was the only product detected from similar treatment of *N*-phenylbenzotriazole. Linear naphthotriazole was photolytically transformed into β -naphthylamine but a methoxy derivative could not be found. Angular naphthotriazole gave no identifiable photolytic product. *v*-Triazolo[1,5-*a*]pyridine underwent photolysis in methanol to give α -picoline, α -picolylmethyl ether and α -picolylmethanol in low yield. A similar photolysis in acetic acid afforded α -pyridylmethyl acetate. The mechanisms for the formations of products are discussed.

Phenylcyanocarbene (3), an assumed intermediate for the formation of phenylacetonitrile (4) by hydrogen abstraction and for α -methoxyphenylacetonitrile (5) by insertion, was brought about by the photoelimination of nitrogen and hydrogen bromide from 4-phenyl-5-bromo-1,2,3-triazole (1) in methanol. On the other hand the formation of phenylacetonitrile (4), the preferred tautomer of phenylketimine (7), may have required a rearrangement converted with or following the photoelimination of nitrogen from 3-phenyltriazole (6) (2).

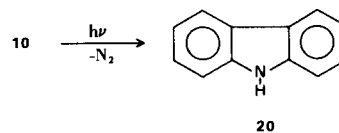
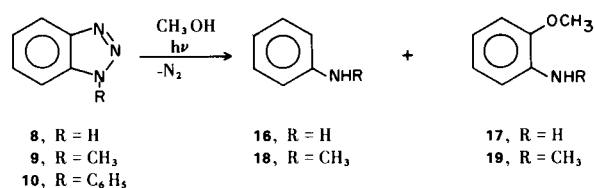


Similar photoelimination from a benzotriazole would require either than an intermediate carbene function be derived from a benzene ring carbon atom or a change in ring size (3,4). This report, in part, describes preliminary results of an investigation on the photolysis of benzotriazole (8), its *N*-methyl- (9) and *N*-phenyl- (10) derivatives, 1*H*-naphtho[2,3-*d*]triazole (11) and 3*H*-naphtho[1,2-*d*]triazole (12).

Based on the recognition (3) of probable intercon-

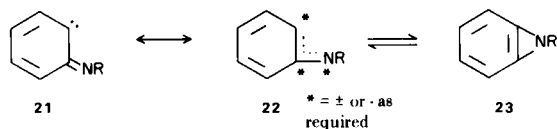
version between α -pyridylcarbene (14) and phenylnitrene (15), the photolysis of *v*-triazolo[1,5-*a*]pyridine (13) in which ring-fusion atoms are C,N rather than C,C, has also been investigated, not only for an expected transformation into the intermediate carbene (14) and its subsequent reactions, but also for possible rearrangements (3,4).

Irradiation in methanol at 3000Å slowly transformed benzotriazole (8) into aniline (16) and *o*-anisidine (17) in low yield. After a similar lengthy irradiation *N*-methylbenzotriazole (9) gave a high yield of *N*-methylaniline (18) and a very low yield of *N*-methyl-*o*-anisidine (19). In contrast the only product identified after similar irradiation of *N*-phenylbenzotriazole (10) was carbazole (20) formed in high yield (5).

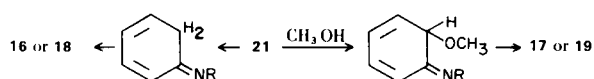


Although formation of the amines (16 and 18) by hydrogen abstraction, the anisidines (17 and 19) by insertion into the OH bond in methanol, and carbazole (20) by intramolecular insertion into a CH bond are characteristic reactions of an intermediate carbene (21)

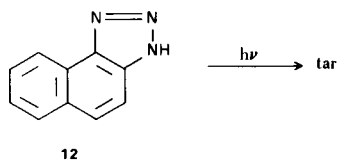
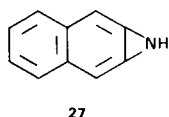
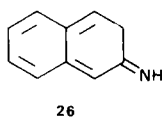
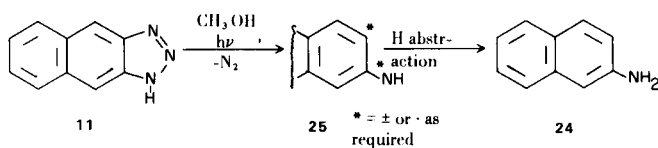
(6), each of the products may, in principle, be derived from either an electron delocalized intermediate (22) or a benzazirine (23) (7). A lack of evidence for contraction of the benzene ring by rearrangement may reflect the absence of an intermediate diazo compound (8).



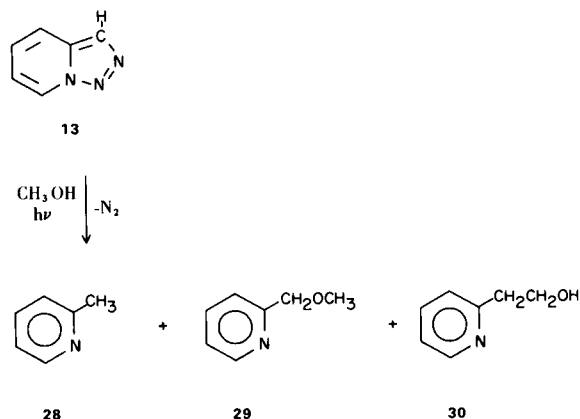
a, R = H; b, R = CH₃; c, R = C₆H₅



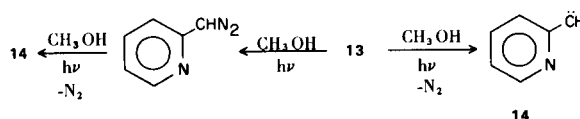
The formation of β -naphthylamine (24) in low yield and the apparent absence of formation of a methoxy derivative by the irradiation of 1*H*-naphtho[2,3-*d*]triazole (11) are consistent with the intermediacy of a 1,3-diradical or zwitterion (25) but discount the energetically less favorable carbene (26) and azirine (27). Irradiation of the isomeric naphthotriazole (12) gave only an intractable tar.



Ring transformation was not detected after irradiation of pyridotriazole (13) (9) in methanol. In low yield α -picoline (28), α -picolylmethyl ether (29), and α -picolylmethanol (30) were formed.



Supporting the intermediacy of α -pyridyl carbene (14) is the formation of 28 by intermolecular hydrogen abstraction, 29 by insertion into an OH bond, and 30 by insertion into a CH bond of methanol. A choice between simultaneous or sequential cleavage of two triazole ring bonds has not been made. Photolysis in acetic acid transforms pyridotriazole (13) into α -pyridylmethyl acetate (10) in 39% yield and trace amounts of α -picoline.



EXPERIMENTAL (11)

Benzotriazole (8) is commercially available. Its *N*-methyl- (9) (12) and *N*-phenyl- (10) (13) derivatives, naphtho[2,3-*d*]triazole (11) (14), naphtho[1,2-*d*]triazole (12) (15), and ν -triazolo[1,5-*a*]pyridine (13) (16) were prepared as reported.

Photolysis of Benzotriazole (8).

A solution of benzotriazole (8) (1.19 g., 10 mmoles) in 500 ml. of absolute methanol, was irradiated for sixty hours by 3000Å lamps. The presence of starting-material was periodically checked by NMR and after 60 hours of irradiation it could not be detected. A brown resin left after solvent removal was chromatographically separated by a silica column (12 in. by 1 in.). Chloroform (150 ml.) eluted 110 mg. of a pale yellow liquid, identified by comparison of gc retention times with authentic samples, on a carbowax column, as a mixture of aniline (16), 1.6% yield and *o*-anisidine (17), 8.2% yield. Mass spectra for samples obtained directly from the gc showed the expected molecular ions at M 93 (aniline) and M 123 (*o*-anisidine) as well as the known respective fragmentation patterns. Further analysis of this product fraction gave NMR (carbon tetrachloride) at δ 3.63 (broad singlet, NH₂ and OCH₃), 6.65 (s, C₆H₄(OCH₃)NH₂) and 6.70 (multiplet, C₆H₅NH₂).

An unidentified dark resin, 230 mg., was obtained on further elution with chloroform (300 ml.) and a tar remained on top of the column.

Photolysis of 1-Methylbenzotriazole (9).

A solution of 1-methylbenzotriazole (9) (1.33 g., 10 mmoles)

in 500 ml. of absolute methanol was irradiated for 40 hours with 3000Å lamps. The solution was concentrated and the residue was chromatographed through a column of silica gel (12 in. by 1 in.). The earlier elutions with 1:1 mixture of hexane-benzene (800 ml.) gave *N*-methylaniline, (**18**) (350 mg., 63%) and the subsequent elutions with the same mixture (200 ml.) afforded *N*-methyl-*o*-anisidine, (**19**) (27 mg., 3.8%). For *N*-methylaniline, glc. (carbowax column) retention time compared with the authentic sample; IR spectra was identical with that of the authentic sample; NMR (carbon tetrachloride) δ 6.68 (m, 5, C₆H₅), 3.40 (s, 1, NH) and 2.75 (s, 3, N-CH₃); *m/e* 107. For *N*-methyl-*o*-anisidine: IR (carbon tetrachloride) 3460 (m, N-H) and 2830 cm⁻¹ (M, O-CH₃); NMR (carbon tetrachloride) δ 2.75 (s, N-CH₃), 3.42 (s, NH), 3.68 (s, O-CH₃) and 6.70 (m, C₆H₄); *m/e* 137. Further elutions with benzene (500 ml.) gave starting material (0.63 g., 48%).

Photolysis of 1-Phenylbenzotriazole (**10**).

A solution of 1-phenylbenzotriazole (**10**) (1.46 g., 7.5 mmoles) in methanol (500 ml.) was irradiated with 3000Å lamps for 16 hours. The solution was concentrated, the residual solid was triturated with carbon tetrachloride to give a colorless solid (0.76 g.) for which m.p. and mixture m.p. with authentic carbazole was 244-245°. The filtrate was chromatographed over a column of silica gel (12 in. by 1 in.). Benzene elution (350 ml.) gave the unreacted starting material (210 mg., 14%). Benzene-chloroform mixture (2:1), 300 ml., eluted carbazole (60 mg.), m.p. 244-245°. Total yield of carbazole based on the recovered starting material was 78%.

Photolysis of 1*H*-naphtho[2,3-*d*]triazole. (**11**).

A solution of the naphthotriazole (**11**) (0.75 g., 4.4 mmoles) in methanol was irradiated for 4 hours with a 450W high pressure arc lamp. The colorless solid formed during irradiation was collected (300 mg.), m.p. 269-272° with decomposition. The sample could not be characterized owing to its very poor solubility in all organic solvents. The methanol filtrate was concentrated, adsorbed over two tlc silica gel plates (16 in. by 7.5 in.) and developed in a 3:1 benzene-ethyl acetate mixture. The four distinctly separated bands were extracted in chloroform (250 ml. each) and subsequently freed from the solvent. Only one band gave almost colorless crystals of β -naphthylamine (32 mg., 4.9%) m.p. and mixture m.p., 110-110.5°. The IR and NMR spectra were also superimposable with those of the authentic sample. The other bands gave only trace amounts of resinous products, the micro NMR and IR analyses of each fraction failed to show signals characteristic of any functional group.

Photolysis of ν -Triazolo[1,5-*a*]pyridine (**13**).

After irradiation at 3000Å for 16 hours of 1.19 g. (10 mmoles) or ν -triazolo[1,5-*a*]pyridine (**13**) in 400 ml. of methanol, the product concentrate was chromatographically separated by a silica gel column (12 in. by 1 in.). Ether-petroleum ether (1:1, 600 ml.) eluted a mixture which was separated by gc (Dowfax 9N9/potassium hydroxide, 6 ft. by 0.25 in. column) into α -picoline (**28**), 8 mg., 1.6% yield, α -picolymethyl ether (**29**), 93 mg., 7.5% yield, trace amounts of α -picolymethanol (**30**) (yields are based on recovered starting material), and tar. Authentic samples of α -picoline and α -picolymethanol were shown to be respectively identical with **28** by gc, NMR and mass spectra and with **30** by mass spectra. Identification of the hitherto unknown ether (**29**) is based on IR (carbon tetrachloride) 2820 cm⁻¹ (OCH₃); NMR (carbon tetrachloride) δ 3.36 (s, 3, OCH₃), δ 4.80 (s, 2, ArCH₂O-) and a multiplet centered at δ 7.66 (4, C₅H₄N). The parent peak (M⁺, 123) is seen for both the α -picolymethyl ether (**29**) and the isomeric α -picolymethanol (**30**)

in the mass spectra. Each appears to be converted to α -picoline (**28**) (*m/e* 93) and the fragmentation peaks for **28** are also found for **29** and **30**. In addition to the loss of 30 mass units, corresponding to an elimination of formaldehyde, the latter (**30**) also loses 18 mass units, presumably the result of dehydration to α -vinylpyridine (*m/e* 105), from which a definitive fragment (*m/e* 53) assumed to be acrylonitrile is observed. α -Picolymethanol has a gc retention time lower than that for α -picolymethyl ether. It was not obtained in sufficient quantity for further characterization.

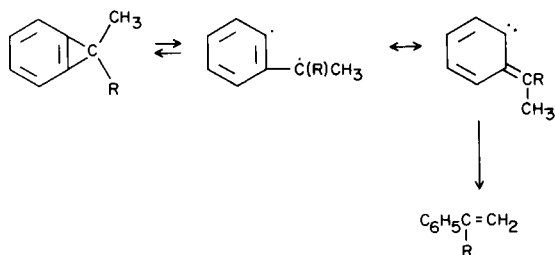
Further elution of the silica column with ether (400 ml.) gave unreacted ν -triazolo[1,5-*a*]pyridine (**13**), 480 mg., 40%. A quantity of tar remained on top of the column.

After a solution of 1.19 g. (10 mmoles) of ν -triazolo[1,5-*a*]pyridine (**13**) in 400 ml. of acetic acid was irradiated at 3000Å for 24 hours, the solvent was removed by distillation b.p. 45° (7-8 mm.). Gc separation (silicone GE XE-60, nitrile gum, 6 ft. by 0.25 in.) showed four volatile components in trace amounts. The first was identified as α -picoline but the others have not been identified. A fifth fraction was identified as α -pyridylmethyl acetate. The latter was then isolated from the product concentrate by distillation, b.p. 105° (7-8 mm.), (9), 580 mg., 38.4% yield; IR (neat) 1655 cm⁻¹ (CO₂CH₃); NMR (carbon tetrachloride) δ 7.82 (m, 4, C₅H₄N), 5.12 (s, 2CH₂-O), 2.08 (s, 3, CO₂CH₃). The picrate derivative was prepared, m.p. 167-168° (9). Distillation left a tarry residue.

REFERENCES

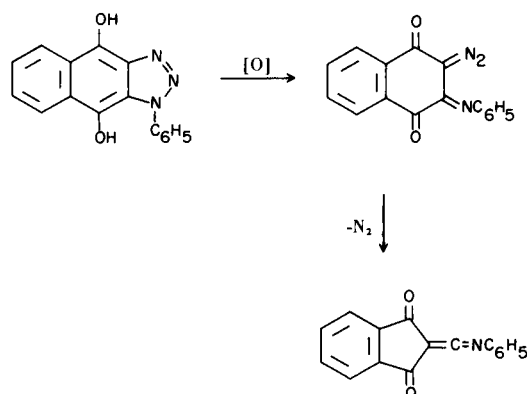
- (1) Financial support was received from DASA grant No. NGr 14-012-004.
- (2) J. H. Boyer and R. Selvarajan, *Tetrahedron Letters*, 47, (1969).
- (3) J. H. Boyer, "Rearrangements Involving Nitrene Intermediates" in "Mechanisms of Molecular Rearrangements", B. S. Thyagarajan, Ed., John Wiley and Sons, Inc., New York, N. Y., 1969, discussed the probable interconversion of a phenyl nitrene and a corresponding α -pyridyl carbene. W. D. Crow and C. Wentrup, *Tetrahedron Letters*, 6149 (1968) report the first demonstration in the thermal interconversion of 2-pyridyl carbene and phenyl nitrene.
- (4) An azepine derivative, available from phenyl nitrene by ring-enlargement, could result if a similar ring-enlargement of α -pyridyl carbene occurred in a nucleophilic solvent.
- (5) E. M. Burgess, R. Carithers and L. McCullagh, *J. Am. Chem. Soc.*, 90, 1923 (1968), reported a nearly quantitative yield.
- (6) Product formation diagnostic for the specific intermediacy of phenyl nitrene, isomeric with the carbene, (**21a**), was not detected. If the photoisomerization of phenyl azide into benzotriazole (R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 64, 160 (1964) is essentially irreversible, formation of phenyl nitrene from the latter may require tautomerization of **21a**. If it is present, then the formation of aniline (**16**), in part may represent hydrogen abstraction by phenyl nitrene and *o*-anisidine (**17**) may result in part from either an unknown photo-substitution in the aromatic ring or an unknown photo-rearrangement of *O*-methyl-*N*-phenylhydroxylamine, the product from phenyl nitrene insertion into the methanolic hydroxyl group. Phenyl nitrene insertion into a methanol CH bond and dehydration would lead to a polymer of the anil of formaldehyde.
- (7) High energy required for the presumed antiaromaticity of a benzazirine (**23**), may preclude its contribution to the equilibrium, **21** \leftrightarrow **22** \rightleftharpoons **23**. G. L. Closs, L. R. Kaplan and V. I. Bendall, *J. Am. Chem. Soc.*, 89, 3376 (1967) suggest an interconversion of a methyl benzocyclopropene with its ring-opened

isomer (a resonance hybrid between a 1,3-diradical and a carbene) and a rearrangement of the latter into an α -substituted styrene:



A similar rearrangement of **21** would give the anil of formaldehyde which would be expected to polymerize.

(8) In a Wolff rearrangement, *o*-diazooxides undergo pyrolytic or photolytic ring-contraction to corresponding derivatives of cyclopentadienecarboxylic acid (P. A. S. Smith and W. L. Berry, *J. Org. Chem.*, **26**, 27 (1961)). A similar rearrangement of an α -diazoketone (J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 42 (1954)) explains ring-contraction products obtained from 1-phenyl-8,9-dihydroxynaphthotriazole (L. Wolff and R. Hercher, *Ann.*, **399**, 274 (1913)).



(9) J. H. Boyer and L. T. Wolford, *J. Am. Chem. Soc.*, **80**, 2741 (1958).

(10) After heating at 100° for 15 minutes in acetic acid *o*-triazolo[1,5-*a*]pyridine (**13**) is transformed into α -pyridylmethyl acetate in 20% yield (9).

(11) Photolytic reactions were carried out at 35° under nitrogen in quartz vessels placed in a Rayonet Chamber Reactor equipped with 16 low pressure mercury lamps. Each charge was degassed by flushing with nitrogen for 8 to 10 hours (unless stated otherwise) prior to irradiation. Infrared spectra were recorded with a Beckman IR 10 spectrophotometer. Nuclear magnetic resonance spectra were taken with a Varian A-60A spectrometer. Mass spectra were recorded with a Perkin-Elmer 270 mass spectrometer. Gas chromatographic analysis were made with Varian aerograph autoprep 700.

(12) F. Krollpfeifer, A. Rosenberg and C. Muhlhauser, *Ann.*, **515**, 113 (1935).

(13) M. Schoff, *Ber.*, **23**, 1839 (1890).

(14) P. Friedlander and S. V. Zakrzewski, *ibid.*, **27**, 761 (1894).

(15) O. Diels, *ibid.*, **54**, 213 (1921).

(16) J. H. Boyer, R. Borgers and L. T. Wolford, *J. Am. Chem. Soc.*, **79**, 678 (1957).

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