Photo- and Thermal Elimination of Nitrogen from
4-Phenyl- and 4,5-Diphenyl-1,2,3-triazole (1)

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Phenylacetonitrile (2) (32%) and small amounts of benzyl methyl ether (3), benzonitrile (5) and methyl benzoate (6) were produced by irradiation of either 4-phenyl-1,2,3-triazole (1) or 4-phenyl-5-deutero-1,2,3-triazole (7) in methanol at 254 nm. In methylene chloride, irradiation of 1 produced 2 (15%) and small amounts of 3,6-diphenyl-1,2,4,5-tetrazine (8). Irradiation of 4,5-diphenyl-1,2,3-triazole (9) in methanol gave 2,4,5-triphenylimidazole (11) (4%) and trace amounts of diphenylacetonitrile (10), benzamide (12), and compounds 3, 5, and 6. Irradiation of 2,3-diphenyl-2H-azirine (13) in methanol gave small amounts of 3, benzaldehyde (4), and compounds 5, 6, 12 as well as 2,3,5,6-tetraphenylpyrazine (14) and in methylene chloride it gave 11 (16%) and small amounts of 4, 5, 14, and acetophenone (15).

On heating 4-phenyl-1,2,3-triazole (1) in n-hexadecane, elimination of nitrogen at 290° left phenylacetonitrile (2) as the only identified product. Similar pyrolysis of 4,5-diphenyl-1,2,3-triazole (9) produced 2,3,5,6-tetraphenylpyrazine (14) along with an intractable material. An efficient thermal isomerization of 2,3-diphenyl-2H-azirine (13) gave 2-phenylindole (17).

Photo-elimination of nitrogen from 4-phenyl-1,2,3-triazole (1) with rearrangement of the residue into phenylacetonitrile (2) was described in an earlier communication (3). Certain other products have now been identified and investigations have been extended to 4-phenyl-5-deutero-1,2,3-triazole (7), 4,5-diphenyl-1,2,3-triazole (9) and to 2,3-diphenyl-2H-azirine (13), an expected intermediate in the photolysis of 9. Thermal elimination of nitrogen from 1 and 9 has also been investigated.
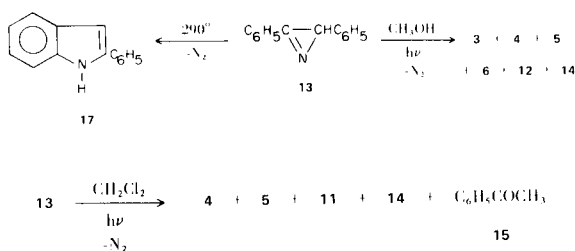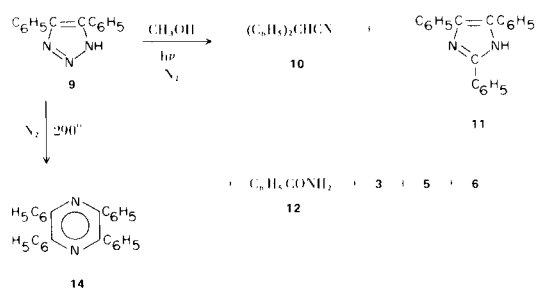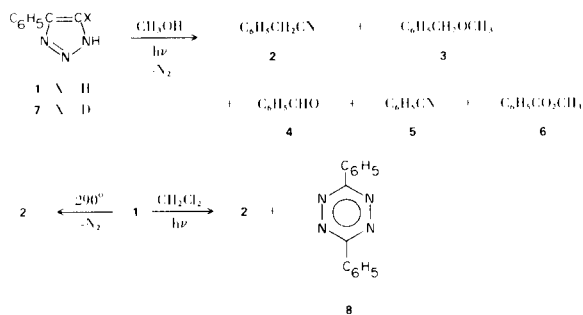
Results.

In addition to phenylacetonitrile (2), the principal product, small amounts of benzyl methyl ether (3), benzonitrile (5), and methyl benzoate (6) were produced by irradiation of either 4-phenyltriazole (1) or its 5-deutero derivative (7) in methanol at 254 nm. A trace of benzaldehyde (4) was also found in the product mixture from 1. Irradiation of 1 in methylene chloride produced 2 in low yield along with trace amounts of 3,6-diphenyl-1,2,4,5-tetrazine (8) and an intractable yellow resin. Similar irradiation of 4,5-diphenyl-1,2,3-triazole (9) in methanol gave very low yields of diphenylacetonitrile (10), 2,4,5-triphenylimidazole (11), benzyl methyl ether (3), benzonitrile (5), methyl benzoate (6) and benzamide (12).

Irradiation of 2,3-diphenyl-2H-azirine (13) in methanol did not produce detectable amounts of either diphenylacetonitrile (10) or 2,4,5-triphenylimidazole (11). It did produce low yields of benzyl methyl ether (3), benzaldehyde (4), benzonitrile (5), methyl benzoate (6), benzamide (12), and 2,3,5,6-tetraphenylpyrazine (14). Irradiation in methylene chloride afforded both 2,4,5-triphenylimidazole (11) in 16 percent yield and small amounts of 2,3,5,6-tetraphenylpyrazine (14), benzaldehyde (4) benzonitrile (5), and acetophenone (15).

Nitrogen evolved from the triazole ring on heating both 4-phenyltriazole (1) and 4,5-diphenyltriazole (9) in n-hexadecane at 290°. The residue formed phenylacetonitrile (2) from one and with dimerization formed 2,3,5,6-tetraphenylpyrazine (14) from the other. Other products in the intractable mixtures were not identified. Some were detected by gc but none could be correlated with products from the corresponding photo-reactions. Thermally 2,3-diphenyl-2H-azirine (13) isomerized into 2-phenylindole (17) but diphenylacetonitrile was not detected (4). Since 17 was not detected as a thermal product from 9, 13 may not be an intermediate in the thermal transformation 9 → 14.
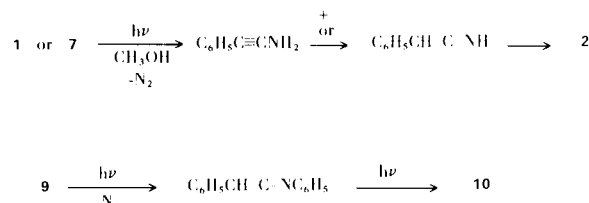
Discussion.

Nmr monitoring revealed that irradiation of **7** in methanol did not bring about an exchange of deuterium with hydrogen attached to the triazole ring insofar as the signal at δ 8.18, characteristic of hydrogen at the 5-position, did not develop. On the other hand, irradiation produced a new signal at δ 3.66 ($C_6H_5CH_2CN$) with intensity dependent on irradiation time. The formation of phenylacetonitrile (**2**) mw 117, was confirmed by ge-mass spectral analysis (m/e 117) which did not detect α-deuterophenylacetonitrile in the product mixture.

The report (5) that irradiation of the latter does not produce phenylacetonitrile is now supported by the failure of irradiation of 2,3-diphenyl-2*H*-azirine (**13**) to produce diphenylacetonitrile (**10**).

The final step, photoisomerization of a ketenimine into a nitrile, has been established (6,7). While a similar stepwise migration of phenyl from carbon to nitrogen to carbon would isomerize the residue after photoelimination of nitrogen from 4,5-diphenyltriazole into diphenylaceto-nitrile (**10**), formation of the latter by a direct migration of phenyl from carbon has not been eliminated.

Fragmentation of both 4-phenyltriazole (**1**) and diphenyltriazole (**9**) produced benzonitrile (**5**), and presumably, phenyl carbene. Insertion of the carbene into methanol accounts for the formation of benzyl methyl ether (**3**) and carbene oxidation accounts for benzaldehyde (**4**).

In addition to phenylacetonitrile (**2**) irradiation of 4-phenyltriazole (**1**) in methylene chloride produced 3,6-diphenyltetrazine (**8**), recently obtained by the irradiation of 5-phenyltetrazole (**8**). It is apparent that the formation of **8** in each of the two reactions may proceed from benzonitrilimine, available from **1** by photoelimination of hydrogen cyanide and from 5-phenyltetrazole by elimination of nitrogen.

Products diagnostic of styryl nitrene and/or its valence isomeric azirine **9** were not found when **1** was irradiated in methanol. But similar irradiation of **9** may have proceeded with stepwise fragmentation into a nitrene or an azirine, since the product, 2,4,5-triphenylimidazole (**11**), also resulted from the irradiation of 2,3-diphenyl-2*H*-azirine (**13**) in methylene chloride. The formation of both the imidazole (**11**) and 2,3,5,6-tetraphenylpyrazine (**14**) from **13** tend to support an intermediate formal dimer **16** of 2,3-diphenyl-2*H*-azirine (**13**) (10). Valence isomeri-
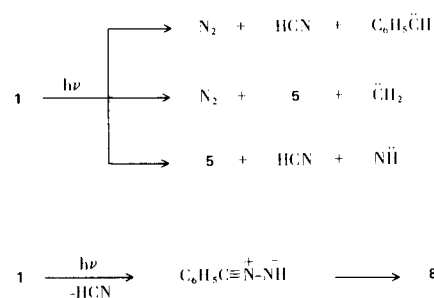
The loss of deuterium confirms the absence of intra-molecular migration of hydrogen from carbon to carbon and therefore tends to support the intermediacy of phenylethynylamine and/or phenylketenimine. Either would lose deuterium as it migrates by rapidly exchanging with the alcoholic proton of the solvent. Apparently, rearrangement to an ynamine and/or a ketenimine is con-verted with nitrogen evolution since otherwise an unre-arranged residue would cyclize into 3-phenyl-2*H*-azirine.

zation and hydrogen expulsion affords **14** while the trans-formation into **11** requires an expulsion of phenyl carbene.

In the thermolysis of triazole (**9**) the intermediacy of azirine (**13**) is unlikely since the thermal reactions **9 → 14** and **13 → 17** were observed while **9 → 17** and **13 → 14** were not. Perhaps a thermal interaction between two molecules of diphenyltriazole (**9**) leads directly to the formation of the pyrazine (**14**) or its precursor, e.g., **16**. Clarification by further investigation is planned.

Elimination of the possible formation of the imidazole (**11**) by a dipolar addition of benzonitrile to diphenyl-azirine (or its valence tautomer β-(β-phenyl)styryl nitrene) is based on the inability of p-anisonitrile to produce a p-methoxyphenyldiphenylimidazole in the product mixture when irradiation of diphenylazirine was conducted in the presence of an excess p-anisonitrile; only triphenylimid-azole (**11**) was formed. An explanation for the formation of methyl benzoate (**6**) from **1** and acetophenone (**15**) from **13** cannot be offered at this time.

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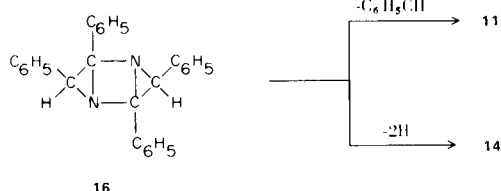
EXPERIMENTAL

After each charge was degassed by flushing with nitrogen for 8 to 10 hours (unless stated otherwise), irradiation at 254 nm was carried out at 35° under nitrogen in a Rayonet chamber reactor with 16 low pressure mercury lamps. Instrumental data were obtained from a Perkin-Elmer 237-B infrared spectrophotometer, a Varian A-60A nmr spectrometer, a Cary-14 ultraviolet spectro-meter, a Perkin-Elmer 270 mass spectrometer and a Varian-Aero-graph 1800 gas chromatograph. The adsorbent in column chromato-graphy was silica gel. Each yield is based on recovered starting material. Each compound was identified by direct comparison with authentic data provided by gc, uv, ir, mass spectra, nmr and mixture m.p.

4-Phenyl-5-deutero-1,2,3-triazole (7).

A mixture of 4.0 g. (39 mmoles) of phenylacetylene-d (**11**) and 3.8 g. (33 mmoles) of trimethylsilyl azide was heated for 24 hours at 110° and then for 24 hours at 170° in an autoclave. After cooling the product mixture treated with 100 ml. of water gave a pale yellow solid. It separated twice from chloroform-hexane mixture as colorless glistening crystals of 4-phenyl-5-deutero-1,2,3-triazole (4.4 g., 92%), m.p. 145-146°; ir (potassium bromide) 3550-3400 (broad, NH), 1460 (m), 1370 (w), 1310 (w), 1210 (m), 1080 (m), 1020 (s), 990 (w), 970 (s), 920 (w), 850 (s), 780 (m), 740 (s), and 695 cm^{-1} (s); nmr (acetone-d$_6$): δ 3.20 (broad, NH), 7.30-8.00 (multiplet, 5H, phenyl); mass spectrum m/e 146 (M$^+$).

Photolysis of 4-phenyl-1,2,3-triazole (1) in Methanol.

A degassed solution of 1.0 g. (6.9 mmoles) of the triazole (12) in 400 ml. of anhydrous methanol was irradiated for 110 hours at 2537A as a change was monitored by nmr. The solvent was re-moved and the brown viscous residue (0.852 g.) was analyzed by gc (15% carbowax, 6′ x 1/8″, temperature programmed) with added ethyl benzoate as an internal standard. The following products, in their order of appearance, were obtained: benzyl methyl ether (10.1 mg., 1.2%), benzaldehyde (2.05 mg., 0.28%), benzonitrile (2.0 mg., 0.28%), methyl benzoate (10.12 mg., 1.08%), acetophenone (1.2 mg., 0.12%) and phenylacetonitrile (260 mg., 32.11%). Gc (15% carbowax, 6′ x 1/8″)-mass spectrum analysis also detected benzyl methyl ether (M$^+$ 122), benzaldehyde (M$^+$ 106), benzonitrile (M$^+$ 103, methyl benzoate (M$^+$ 136), aceto-phenone (M$^+$ 120) and phenylacetonitrile (M$^+$ 117). The residual mixture was then chromatographed over silica gel (12″ x 1″). A pale yellow liquid was eluted by 300 ml. of hexane-benzene (2:1) followed by 300 ml. of hexane-benzene (1:1) and found by gc to be a mixture of the above six volatile components. Further elutions with benzene-ether, ether-ethyl acetate, ethyl acetate-ethanol mixtures gave intractable material.

Similar reactions (compound No., mg; solvent, ml.; irradia-tion time, h/product No., (a) mg; isolation method; (b) yield %):

1, 1000; dichloromethane, 500; 64/**2**, 45.0; col; 14.7/**8**, 12.0; col; 1.5/yellow resin; col; —/**1**, 310; col; 30.3 (13).

7, 1020; methanol, 400; 40/**3**, 12.3; gc; (c) 1.4/**5**, 4.0; gc; (c) 0.5/**6**, 14.3; gc; (c) 1.5/**2**, 247.4; gc; (c) 30.2/**7**, 264.0; col; (d) 26.0/resin; col.

9, 1050; methanol, 300; 54/**3**, 0.6; gc; (c) 0.1/**5**, 9.6; gc; (c) 1.9/**6**, 26; gc; (c) 3.8/**10**, 6.8; col; (e) 0.7/**11**, 26; col; (e) 3.5/**12**, 18; col; (e) 3.8 (14).

13, 965; methanol, 500; 48/**3**, 3.0; gc; (c) 0.5/**4**, 21.2; gc; (c) 4.0/**5**, 4.2; gc; (c) 0.8/**6**, 12.3; gc; (c) 1.8/**14**, 16.0; col; (e) 1.65/**12**, 8.0; col; (e) 1.3 (15,16).

13, 498; dichloromethane, 250; 18/**4**, 15.1; gc; (c,f) 5.5/**5**, 6.7; gc; (c,f) 2.6/**15**, trace; gc; (c,f) —/**14**, 4; col; 0.8/**13**, 60.0; col; 16.2. Two major and three minor components detected by gc remain unidentified.

(a) Listed in the order of isolation. (b) Gas chromatography (gc) or column chromatography (col). For col the eluents increased in polarity from mixtures of paraffin hydrocarbons and benzene to alcohols. (c) 15% apiezon-L, 5′ by 0.25″, with ethyl benzoate as internal standard, 130°, 20 psi. (d) Eluted with benzene-ether. (e) Neutral alumina, 12″ by 1″. Eluents increased in polarity from mixtures of hydrocarbons to esters. (f) Benzyl ethyl ether internal standard.

Pyrolysis of 4-Phenyl-1,2,3-triazole (1) in n-Hexadecane.

A solution of 500 mg. (3.45 mmoles) of the triazole in 25 ml. of anhydrous n-hexadecane was refluxed at 290° and the reaction was monitored by tlc. After heating for 16 hours, a dark brown color developed and the reaction was stopped. The reaction mix-ture was analyzed by gc (carbowax 15%, 6′ x 1/8″, 130°, 25 psi). Of two volatile components with the same intensity one was characterized as phenylacetonitrile (14.3%) while the other com-ponent could not be identified. To the reaction mixture a large excess of hexane (400 ml.) was added to precipitate the unreacted starting material, 300 mg., 60%.

Similar reactions (compound No., mg; solvent, ml; reaction temperature time, h/product No., mg; isolation method; yield %):

9, 132; hexadecane, 10; 290, 30/**14**, 6.0; col; 5.6/**9**, 4.0; col; 3.0.

13, 250; hexadecane, 25; 290, 8/17, 135.0; —; 54.0. The product was recrystallized from the concentrated reaction mixture by benzene-hexane. The filtrate contained tarry material.

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(2) Author to whom correspondence should be sent.

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(5) A. Hassner and F. W. Fowler, J. Am. Chem. Soc., 90, 2869 (1968) reported the photogeneration of 3-phenyl-2H-azirine and 3-methyl-2-phenyl-2H-azirine. Apparently isomerization of an azirine into a nitrile did not occur.

(6) Cyclization between ortho positions of the two adjacent phenyl substituents in 9 to produce a dihydrophenanthrene derivative was not observed. Presumably detection would depend upon subsequent conversion into a phenanthrene derivative and the latter would be inhibited or unexpected in the absence of oxygen. Degassing apparently removed nearly all of the oxygen

in the present work since no oxidation products were obtained from 7 and 9; benzaldehyde was obtained from 1 and 13.

(7) L. A. Singer and P. D. Bartlett, Tetrahedron Letters, 1887 (1964) reported the photoisomerization of a ketenimine into a nitrile.

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