

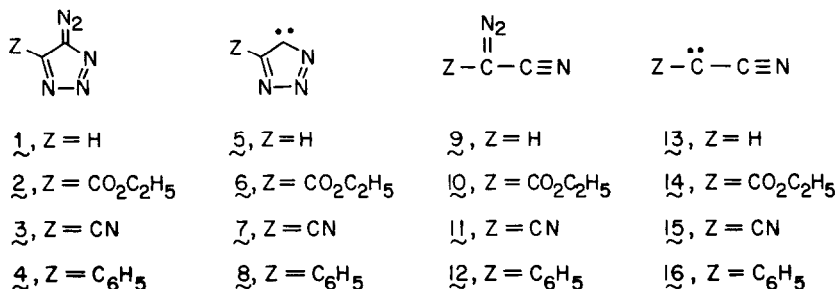
THERMOLYSIS AND PHOTOLYSIS OF 4-DIAZO-1,2,3-TRIAZOLES IN BENZENOID SOLVENTS, SYSTEMS WHICH  
 REVEAL DECOMPOSITION OF DIAZO COMPOUNDS TO CARBENES TO DIAZO COMPOUNDS TO CARBENES

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Abstract 4-Diazo-1,2,3-triazoles thermolyze and photolyze to 4H-1,2,3-triazolyliidenes which (1) convert benzenes to 4-phenyl-1,2,3-triazoles or/and (2) isomerize to  $\alpha$ -diazonitriles which react carbenically with benzenes by addition, ring-expansion or substitution processes

Azolyliidenes are carbenic derivatives of cyclopentadienyliidene containing one or more nitrogen atoms in their conjugated 5-membered ring systems. Azolyliidenes such as 2,5-diphenyl-3H-pyrrolyliidene,<sup>1a</sup> 2H-imidazolyliidene<sup>1b</sup> and 5-t-butyl-3H-pyrazolyliidene,<sup>1c,d</sup> as generated from their corresponding diazoazoles, are highly electrophilic and have been of interest with respect to substitution and/or ring-expansion of aromatic substrates. We now report synthesis of 4-diazo-1,2,3-triazoles 1-4<sup>2a-c</sup> and the reactions of 4H-1,2,3-triazolyliidenes 5-8 in the presence of various benzenes. The present systems reveal that (1) photolysis of 4-diazo-1,2,3-triazoles

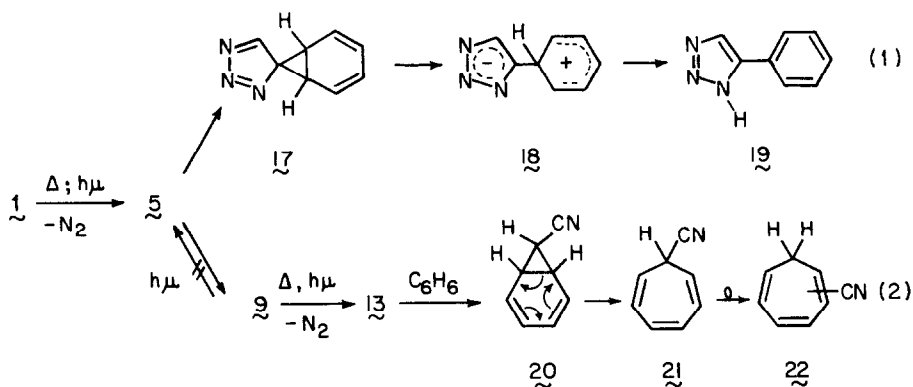


results in different behavior than thermolysis, (2) 4H-1,2,3-triazolyliidenes effect substitution rather than ring-expansion of benzenoid substrates and, most interestingly, (3) 4H-1,2,3-triazolyliidenes (5-8) isomerize to  $\alpha$ -diazonitriles (9-12) that decompose to  $\alpha$ -cyanocarbenes (13-16) which then react with benzenes by addition, ring-expansion and/or substitution processes. Upon use of thermal methods as will be illustrated, decomposition of 1-4 in benzenic environments is an effective synthesis of 4-phenyl-1,2,3-triazoles.

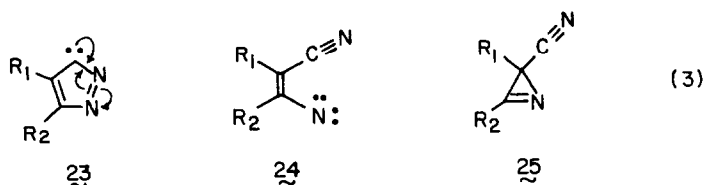
Diazotriazoles 1-4<sup>2a-c</sup> are prepared by diazotization of their corresponding amines in dilute hydrochloric acid with sodium nitrite at 0°C, neutralization with sodium carbonate, repeated extractions with dichloromethane, storage over magnesium sulfate and careful removal of the dichloromethane. The diazotriazoles are light-sensitive solids which explode violently at their melting points but are handleable in solution or, with care, in suspension in various solvents. For safety, 1-4 were transferred as concentrated solutions in dichloromethane, the reaction substrate was added and the dichloromethane was totally removed under reduced pressure.

Thermolysis of 1 in suspension in refluxing benzene for >6 hours and chromatography on silica gel yields 4-phenyl-1,2,3-triazole (19, 53%) and a mixture of isomeric cyanocyclohepta-

trienes (21 and 22, 15%) Photolysis of 1 suspended in benzene occurs smoothly (<3 hours) but differs significantly in that 19 and 21-22 are formed in 26 and 54% yields, respectively <sup>2d</sup> Triazole 19 is identical with an authentic sample and is presumably formed by thermal and photolytic conversions of 1 to 4H-1,2,3-triazolylidene (5) which effects substitution of benzene as in 17-19 Cyanocycloheptatrienes 21-22 are identifiable from their IR and NMR spectra and by comparison with 21-22 as prepared by irradiation of  $\alpha$ -diazocetonitrile (9) in benzene <sup>2e</sup> Forma-

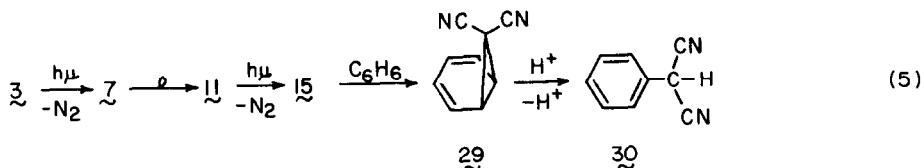
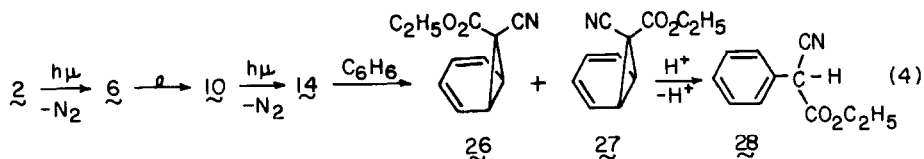


tion of 21-22 presumably occurs upon conversion of 5 to 9 and then cyanocarbene (13) which adds to benzene followed by ring-expansion of 20 and sigmatropic rearrangements of hydrogen Triazole 19 is thermally and photochemically inert under the above conditions for reactions of 1 with benzene <sup>2f</sup> and 9 does not revert photolytically to 5 which then converts benzene to 19 <sup>2e</sup> That irradiation of 1 in benzene leads to more 21-22 and less 19 than in thermolysis is presently interpretable on the basis that generation of excited 1 enhances collapse to 9. Sampling of mixtures of 1 and benzene at various stages of photolysis reveals weak bands at 2240 and 2100  $\text{cm}^{-1}$  assignable to  $\text{C}\equiv\text{N}$  and  $\text{C}=\text{N}=\text{N}$  IR absorptions of 9 Conditions were not found however for preparative conversion of 1 to 9 Collapse of a 4H-1,2,3-triazolylidene (5) to an  $\alpha$ -diazonitrile (9) is a new reaction The new reaction involves cleavage of the azo moiety in 5 and is analogous to isomerization of a 3H-pyrazolylidene (23) via 24 to a 2H-azirine (25, Eq 3) <sup>1c</sup> Transformation of 1 to 13 is also doubly delightful in that conversion of a diazo compound (1) to a carbene (5) to a diazo compound (9) to a carbene (13) is involved



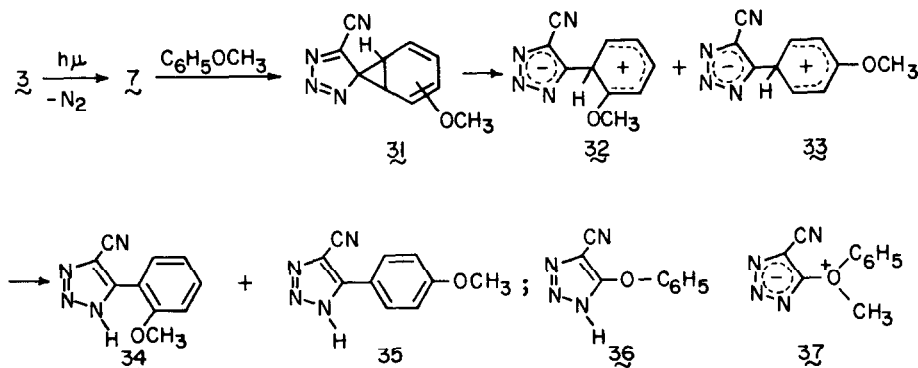
Decomposition of 2 and 3 in benzenoid environments was then investigated Irradiation of 2 in suspension in benzene gives 7-carbomethoxy-7-cyanonorcaradienes 26 and 27 exclusively Chromatography on silica gel results in extensive isomerization of the 26 and 27 and final isolation of 26-27 and ethyl  $\alpha$ -phenylcyanoacetate (28) in 23 and 58% yields, respectively In behavior resembling 2, photolysis of 3 suspended in benzene and chromatography yield 7,7-dicyanonorcaradi-

diene (29, 28%) and phenylmalononitrile (30, 43%). Norcaradienes 26-27 are assigned from their spectra and by NMR comparison with the product from methyl diazocycloacetate and benzene.<sup>2g</sup>



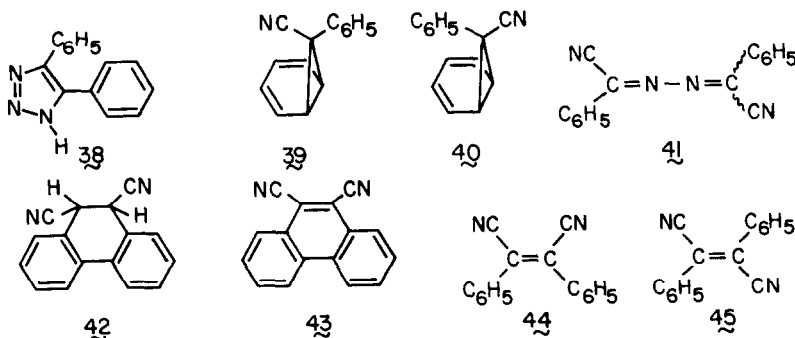
Cyano ester 28, norcaradiene 29<sup>2g</sup> and dinitrile 30 are identical with established products. Irradiation of 2 and 3 in benzene thus apparently indicates that 5-carbomethoxy-4H-1,2,3-triazolylidene (6) and 5-cyano-4H-1,2,3-triazolylidene (7) rearrange faster to 10 and 11, respectively, than they attack the aromatic solvent.

It was then of interest to see if 7, as generated thermally from 3, could be intercepted. Indeed, heating 3 in anisole at 65°C for 5 hours and chromatographic separation yields 4-cyano-5-(2-methoxyphenyl)-1,2,3-triazole (34, 28%), 4-cyano-4-(4-methoxyphenyl)-1,2,3-triazole (35, 21%), 4-cyano-5-phenoxy-1,2,3-triazole (36, 12%) and intractables. Products from 11 are not observed. Assignments of 35-36 are based on elemental, mass spectral, IR and NMR analyses and literature data.<sup>2h</sup> Capture of 7 as a highly electrophilic singlet by anisole, substituent-controlled collapse of spironorcaradienes 31 and hydrogen migration in 32 and 33 account for 34 and 35. Formation of 4-cyano-5-phenoxy-1,2,3-triazole (36) has precedent<sup>2i</sup> and may involve oxygen ylide 37. The demethylation process however has not yet been established.<sup>2i</sup>



Of additional mechanistic significance is that photolysis of 4-diazo-5-phenyl-1,2,3-triazole (4) in benzene for 3 hours and chromatography results in 4,5-diphenyl-1,2,3-triazole (38), isomeric 7-cyano-7-phenylnorcaradienes (39-40),<sup>2g</sup> benzoyl cyanide azines (41),<sup>2j</sup> (E)-9,10-dicyano-9,10-dihydrophenanthrene (42)<sup>2k,1</sup> and 9,10-dicyanophenanthrene (43)<sup>2k,1</sup> in 13, 38, 5, 8

and 11% yields, respectively.<sup>2m</sup> Substitution of benzene by 8 and addition of 16 to benzene account for 38 and for 39-40, respectively. Strong support for 12 as a reaction intermediate is isolation of 41. Also, 42 and 43 are known photo- and photo-oxidation products of (Z) and (E)-dicyanostilbenes (44-45), an olefinic mixture derivable from 12<sup>2n,o</sup>. Further, decomposition of 4 in refluxing benzene for 60 hours results in an increased yield of 38 (>28%) and an additional product, 19 (11%). The thermal behavior of 4 thus parallels that of 1-3 in that carbenic carbenic substitution of benzene by a 4H-1,2,3-triazolyldene (8) is more pronounced upon thermal than upon photolytic generation. Formation of 19 in the thermolysis experiment also raises the question as to the role of triplet 8 in the mechanistic series.



Study of the roles of photosensitizers, light energy, solubility and medium effects on the reactions of 1-4 with varied substituted benzenes is in progress.<sup>2p</sup>

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#### References and Footnotes

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- (a) Y F Shealy, R F Struck, L B. Holum and J A Montgomery, *J Org Chem*, 26, 2396 (1961) have reported synthesis and the properties of 4-carboxamido-5-diazo-1,2,3-triazole (b) 1, mp(dec) 125-126°C, 2, mp(dec) 142-144°C, 3, mp(dec) 131-132°C, 4, mp(dec) 134-135°C (c) For preparation of the amine precursors of 1-4 see (1) P N Newman, *Heterocyclic Chem.* 7, 1159 (1970), (2) D Stadler, W. Anschutz and M Regitz, *Liebig's Ann Chem*, 12, 2159 (1975), (3) J R Hoover and A R Day, *J Am Chem Soc*, 78, 5832 (1956) and (4) D R Sutherland and G Tenant, *J Chem Soc.*, (C), 2156 (1971) (d) All photolyses were conducted under nitrogen with a Hanovia 450 watt medium pressure lamp in a pyrex well (e) M J. S Dewar and R Petit, *J Chem Soc*, 2026 (1956) In further study of this photolysis system in this laboratory, 19 has not been found to be a reaction product (f) For description of the photolytic behavior of 19, see J H Boyer and R Selvarajan, *J Am Chem Soc*, 91, 6122 (1969) (g) E Ciganek, *ibid*, 89, 1454 (1967) (h) G Beck and D Gunther, *Chem Ber*, 2758 (1973) (i) V Franzen and L Fikentschen, *Liebig's Ann. Chem*, 617, 1 (1958), W. Kirmse, "Carbene Chemistry", 2nd Ed, Academic Press, 1971, p 430, M Nair, Ph D Dissertation, The Ohio State University, 1979 (j) T L Gilchrist, G E Gymer and C W Rees, *J. Chem Soc, Perkin Trans (I)*, 1747 (1975) (k) F. B Mallory, C S Wood, J T Gordon, L C. Linquist and M L Savitz, *J Am Chem Soc*, 84, 4361 (1962) (l) M V. Sargent and C J. Timmons, *ibid*, 85, 2186 (1963) (m) An unassigned product, C<sub>22</sub>H<sub>16</sub>N<sub>2</sub> (mp 278-280°C), is also obtained (13%) (n) E Ciganek, *ibid*, 93, 2207 (1971) reports thermolysis of 12 to give products that appear to be "dimers" of 16 (o) Photolysis of phenylethynyl azide has also been found by ref 2f to give 44 and 45, presumably via 16 (p) The mechanistic details of photo-excitation of 1-4 will be discussed upon completion of these studies

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