# PRODUCT FORMATION IN TETRAZOLE PHOTOLYSIS

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Abstract—NMR and ^{15}N-labelling techniques have been used to investigate the photolysis of 5-phenyl-tetrazole (1). Nitrogen is expelled exclusively from positions 3 and 4 of the tetrazole ring. As a consequence of H-bonding, 1,2-dihydro-3,6-diphenyl-1,2,4,5-tetrazine (2) is formed in high yield. Other tetrazoles behave in a similar manner. Photolysis of 2 gave 3,5-diphenyl-1,2,4-triazole (3) and benzonitrile. A photo-induced valence isomerization, followed by photo and thermal steps, is suggested to account for 3. Benzonitrile results from photodecomposition of 3,6-diphenyl-1,2,4,5-tetrazine (8a) a general reaction of *s*-tetrazines. *v*-Triazole formation in the photolysis of 2,5-diphenyltetrazole is also discussed.

A Previous paper[1] compared the photodecomposition of 5-phenyltetrazole (1) with that of its anion, 5-phenyltetrazolide. While the anion, and 5-substituted tetrazolide salts in general,[2] photolyzed to a carbene intermediate, an entirely different reaction occurred with the tetrazole (Eq. 1). Further investigation has clarified the nature of product formation from 1 and other tetrazoles, and revealed new photochemical transformations in the heterocyclic series. The primary product of 5-phenyltetrazole (1) photolysis is 1,2-dihydro-3,6-diphenyl-*s*-tetrazine (2)[1] Secondary photoreactions
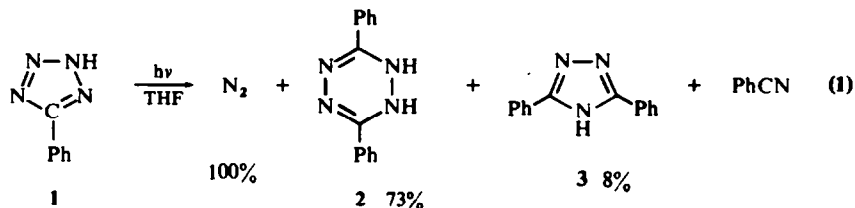

of 2 produce triazole 3 and traces of benzonitrile. The origin of each of these products has been examined.

Dihydrotetrazine formation. Dihydrotetrazine 2 is formally a dimer of the fragment PhCN₂H, derived by loss of nitrogen from 5-phenyltetrazole. *A priori*, two general modes of nitrogen loss are possible. (A) Loss of nitrogen might occur from the 3 and 4 positions of the tetrazole nucleus, giving a 1,3-dipolar intermediate (4, Scheme 1). Alternatively, loss of the 2 and 3 nitrogens (B), perhaps *via* the valence isomers benzimidoyl azide, might lead to the formation dihydrotetrazine 2.

Huisgen *et al.*[3] as well as Markgraf *et al.*[4] have viewed 5-phenyltetrazole thermolysis in terms of a benzonitrile imine intermediate (path A, Scheme 1). However, our failure to intercept 4 with a variety of dipolarophiles (benzonitrile, water, olefins)

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SCHEME 1
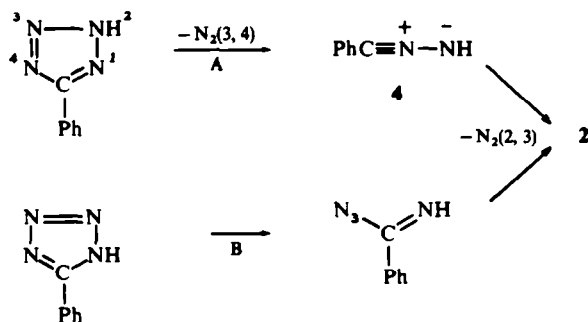
raised doubts concernings its photolytic intermediacy. On the other hand, the familiar tetrazole-imide azide valence isomerization[5] suggested nitrogen loss by path B. It is noteworthy that the preferred tautomer (1H, 2H, or an equilibrium mixture) has never been rigorously established in the 5-substituted tetrazole series.[6]

Paths A and B (Scheme 1) can be distinguished by the extruded nitrogen. Using 5-phenyltetrazole-^{15}N (1 or 4)*, the isotopic distribution of photolytically evolved N_2 was determined. After correction for enrichment and natural abundance, the evolved gas was found to consist of 50 ± 1% $^{28}N_2$ and 50 ± 1% $^{29}N_2$. Thus loss of nitrogen occurs exclusively from positions 3 and 4, and path B (Scheme 1) is inoperative. While consistent with path A, other results cast doubt on the *free* 1,3-dipolar intermediate (4).

Tetrazole photolysis (but not thermolysis[3]) displays a marked specificity for dihydrotetrazine formation. In dipolarophilic media (ethyl fumarate, norbornene) only dihydrotetrazine 2 was isolated. Similarly, photolysis of 1 in either methanol or 70% aqueous tetrahydrofuran produced 2 in ca. 60% yield. Benzoylhydrazine, the product anticipated from the reaction of benzonitrile imine (4) with water, was not detected (VPC) in the aqueous photolysate, although it was found to be stable under the reaction conditions. These results argue against the intermediacy of 4, and contrast with the facile interception of diphenylnitrile imine formed in the photo-decomposition of 2,5-diphenyltetrazole.[1, 7]

It was hoped that NMR analysis of ^{15}N-labeled 5-phenyltetrazoles would resolve the tautomeric ambiguity and establish the ground state structure of the starting material. The position of the proton on the tetrazole ring can be assigned, in principle, by observation of the large ^{15}N-H coupling, $J = 50$–95 Hz.[8] But the spectra (60 Mc, DMSO solvent) of 5-phenyltetrazole-^{15}N (1 or 4), 5-phenyltetrazole-^{15}N (1 or 2), and unlabeled 5-phenyltetrazole all proved identical (Fig. 1). Regardless of either the presence or the location of ^{15}N, *no splitting of the NH signal was observed*. However, the chemical shift of the NH signal (labeled and unlabeled) displayed a marked dependence on both concentration and temperature (Figs 2, 3). The magnitude and direction of these effects are characteristic of protons involved in solute-solute H-bonding.[9, 10]

* One ^{15}N per tetrazole, 91% enrichment. Positions 1 and 4 of 1 are chemically indistinguishable.
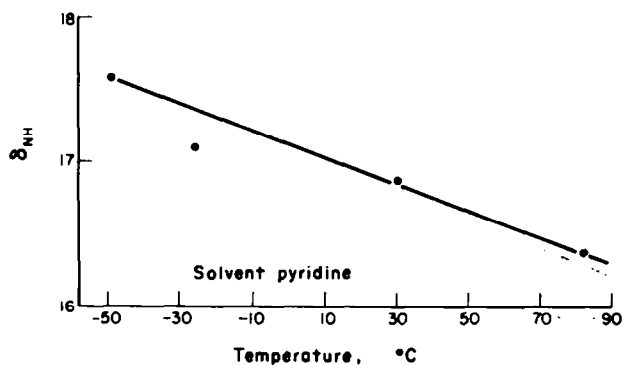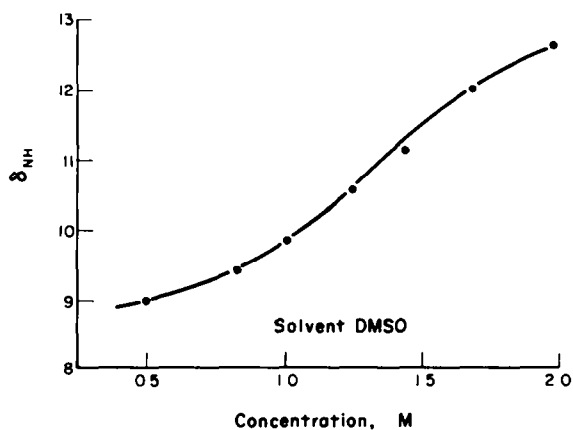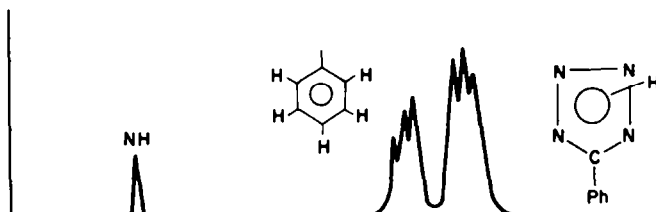
Dilution causes a shift to higher field due to displacement of the equilibrium toward the non-H-bonded form; a similar shift occurs with increased temperature. H-bonding results in lower field resonance.[9] Markgraf[6b] has described similar NMR behavior for 5-methyltetrazole in sulfur dioxide. Due to rapid exchange, the observed

NH signal is averaged over different environments, thus precluding observation of ^{15}N-H splitting. Failure to freeze out the components at $-50°$, particularly in view of the magnitude of ^{15}N-H coupling,[8, 10] indicates a low energy barrier for exchange in the associated tetrazoles.

The NMR data show that **1** exists in solution largely as a H-bonded dimer or higher polymer. It is this property that most probably accounts for the high photolytic preference for dihydrotetrazine formation. Scheme 2 depicts one possible structure for 5-phenyltetrazole dimer, and a plausible reaction sequence leading to product **2**. Similar paths may also be envisaged for other polymeric tetrazole structures.
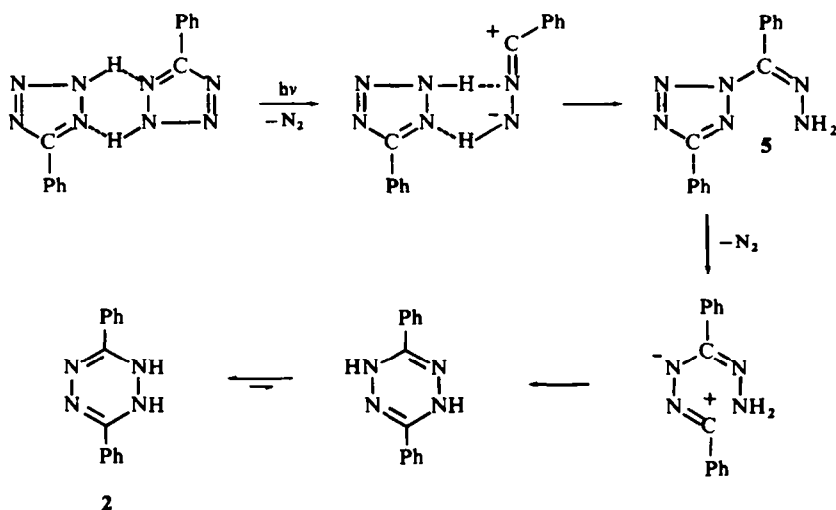
SCHEME 2

Photoexcitation of the dimer causes extrusion of the appropriate nitrogen (N_3—N_4, in accord with the labelling experiments) and produces a 1,3-dipolar intermediate. However, due to H-bonding, this species may be intimately associated with another tetrazole molecule. Internal addition of the tetrazole to the 1,3-dipole would give the hydrazone of 2-benzoyl-5-phenyltetrazole (**5**). In view of the facile thermolysis of 2-benzoyl-5-phenyltetrazole (**6**, never isolated) to 2,5-diphenyl-1,3,4-oxadiazole (**7**),[11] it is likely that **5** would undergo a mechanistically similar decomposition[12] leading to **2**. Such a process might be either thermal or photochemical.[13]

Tetrazole photolysis may serve as a synthetic route to symmetrically 3,6-disubstituted tetrazines (**8**) or their dihydro derivatives. We have obtained acceptable yields of s-tetrazines (Table 1) by this method (Eq. 2), with no attempt to optimize yields.

Triazole formation. Secondary photolysis of dihydrotetrazine (**2**) was shown to produce 3,5-diphenyl-1,2,4-triazole (**3**). We first suggested[1] that this inefficient transformation might occur by fragmentation of **2** to benzonitrile imine (**4**), and subsequent cycloaddition with benzonitrile (Eq. 3). But the presence of added
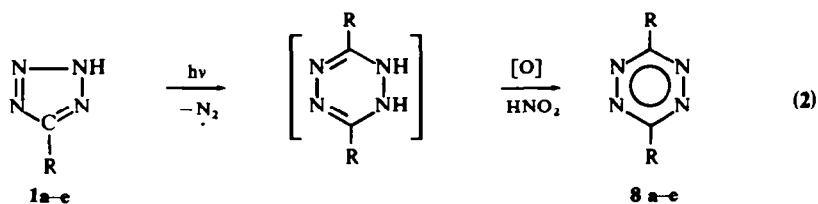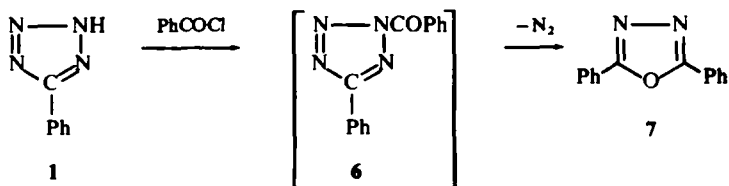
TABLE 1. s-TETRAZINES BY TETRAZOLE PHOTOLYSIS

1	R	Yield 8, %
a	Ph	70
b	PhO	52
c[a]	▷—	42
d[a]	CH₃	39
e	∕∕∕	—[b]

[a] Excess nitrogen evolved: c, 10%; d, 23%. Cyclopropyl nitrile and acetonitrile also formed from 1c and 1d, respectively.

[b] Unstable, polymerizes rapidly at room temperature.
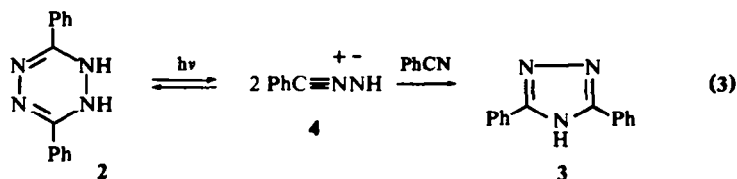
benzonitrile in the photolyses of either 5-phenyltetrazole (**1**) or 1,2-dihydro-3,6-diphenyl-s-tetrazine (**2**) failed to increase the yield of **3**.[14] It is therefore unlikely that **3** is formed as shown in Eq. 3.

Ring opening of 1,3-cyclohexadiene derivatives to conjugated hexatrienes is a

well-recognized photoprocess.[15] Several examples involving heterocyclic systems have recently been reported,[16] and it appears probable that the conversion of **2** to **3** is initiated by reaction in this manner (Scheme 3). Following photo-induced formation of the azo-diimine valence isomer **9**, cyclization and proton shift to aminotriazole **10** might occur. While precedent exists for thermal cyclization,[17] the reaction could, of course, be photochemical in nature (cf. **15** → **16** below). Photolysis of **10** to the indicated radical pair and hydrogen abstraction from the solvent (THF) would then give **3**. Triazole **3** is initially present, to a large extent, as its ammonium salt.
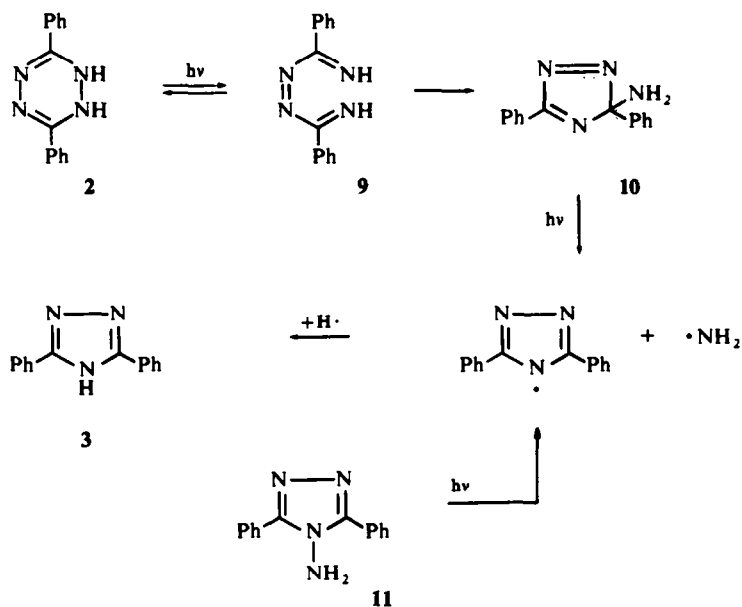

SCHEME 3

In agreement with Scheme 3, a free radical dimer of the solvent (2-(2'-tetrahydro-furanyl)tetrahydrofuran) was isolated. Furthermore, generation of the proposed intermediate radicals by an alternative route, photolysis of 4-amino-3,5-diphenyl-1,2,4-triazole (**11**), gave a 77% yield of **3**. The sequence outlined in Scheme 3 is related to the path postulated by Beak and Miesel[16a] for the photoisomerization of 2,3-dihydropyrazines to imidazoles.

In addition to the dihydrotetrazine (**8b**, Table 1), 3,5-diphenoxy-1,2,4-triazole (20%) and phenol (8%) were obtained from the photolysis of 5-phenoxytetrazole. On the other hand, triazole formation was not observed when 3,6-dicarbethoxy-1,2-dihydro-tetrazine was subjected to prolonged irradiation.

Triazole formation appears to require the 1,2-dihydrotetrazine tautomer. 3,6-Dimethyldihydrotetrazine (**12**) exists in solution as the 1,6-dihydro form.[18] Irradiation of **12** gave no triazole but rather the products shown in Eq. 4. This mode of fragmentation is analogous to that observed with s-tetrazines (below). The trimer (**13**) of ethylidene imine was identified by comparison with an authentic sample.

$$\text{(4)}$$
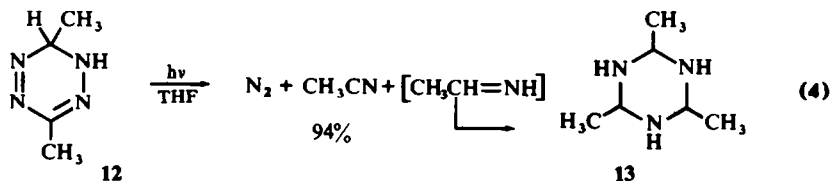
Benzonitrile formation. Small quantities ($< 5\%$) of benzonitrile were detected in the photolyses of both 5-phenyltetrazole (**1**) and 1,2-dihydro-3,6-diphenyl-s-tetrazine (**2**).[1] Despite extensive prepurging with purified nitrogen, a transient red color characteristic of 3,6-diphenyl-s-tetrazine (**8a**) developed in the early stages of reaction. Using freeze-thaw degassing, it was possible to show that the intensity of the red color was directly related to the thoroughness of oxygen removal. Thus it appears that photoexcited dihydrotetrazine (**2**) is readily oxidized to the tetrazine (**8a**) by traces of dissolved oxygen. (Other means of aromatization, e.g., disproportionation, may also be operative.)

These observations prompted investigation of the photolytic behavior of 3,6-diphenyl-s-tetrazine (**8a**) and other tetrazines. Nitrogen (100%) and benzonitrile (92%) were produced. Thus the benzonitrile detected in the photolyses of **1** and **2** probably arises through the photodecomposition of **8a**, formed by *in situ* oxidation of dihydrotetrazine **2**. Similarly, phenol (8%) isolated from the photolysis of 5-phenoxytetrazole may also result from tetrazine photodegradation. Phenyl cyanate, the product anticipated from 3,6-diphenoxy-s-tetrazine (**8b**), is converted to phenol on irradiation in tetrahydrofuran solvent.

$$N_2 + 2\ RCN \qquad \text{(5)}$$
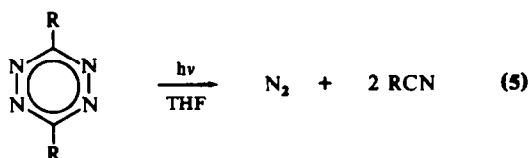
8a: R = Ph
  b: = PhO
  c: = ▷—
  d: = CH$_3$
  f: = CO$_2$C$_2$H$_5$
  g: = CO$_2$CH$_3$

Tetrazines **8c–g** also decomposed according to Eq. 5, indicating a general reaction for this type of heterocycle. Related photofragmentations have been reported for pyrazine[19] and a v-triazine.[20] Thermolysis of **8a** to nitrogen and benzonitrile occurs at 225°.[21]

2,5-*Diphenyltetrazole.* Dihydrotetrazine formation, the major path in 5-mono-substituted tetrazole photolysis, results from H-bonding association of the starting material (Scheme 2). Additional substitution on the tetrazole nucleus or proton ionization[1] obviates such association, giving rise to entirely different chemical

consequences. Photochemical extrusion of nitrogen from 1,5-diphenyltetrazole gives only an intramolecular product (2-phenylbenzimidazole),[22] while diphenyl-nitrile imine is readily trapped by dipolarophiles when 2,5-diphenyltetrazole (14) is irradiated.[1, 7] For comparative purposes, the photolysis of 14 in non-dipolarophilic solvents (THF and benzene) was examined. A reaction involving formal dimerization was again observed, but in this case the major product was a v-triazole, rather than a dihydrotetrazine.

14   15   16, 63%
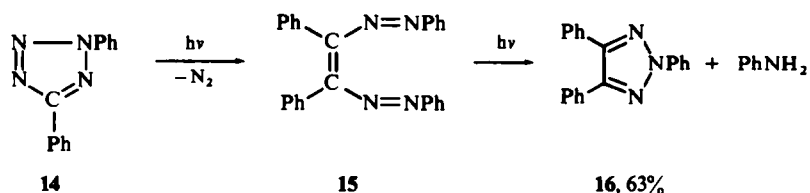
Two products were identified: 2,4,5-triphenyl-1,2,3-triazole (16, 63%) and traces of aniline. Chromatographic analysis of an interrupted run (ca. 40% reaction) provided evidence for the intermediacy of 1,2-bis-phenylazo-1,2-diphenylethylene (15). A small quantity of isolated material showed the infrared spectrum, TLC retention time, and characteristic color of 15. The latter, prepared by oxidation of benzil phenylosazone,[23*] photolyzed in high yield to triazole 16. (Cyclization of 15 to 16 was not effected by prolonged heating in acetic anhydride.)

Formally, 15 is a "head-to-head" dimer of the 1,3-dipole diphenylnitrile imine. But it is unlikely that free 1,3-dipoles are actually involved. A "head-to-tail" mode of dimerization has been described for thermally generated diphenylnitrile imine.[25] Tetrazole-tetrazole association, perhaps photodimerization,† may be responsible for the formation of 15.

Cyclization of 15 to 16 presumably occurs by the photochemical deamination of an azomethine imine intermediate (17). The relationship between valence isomers such as 15 and 17 has been discussed by Curtin and Alexandrou.[26]

17
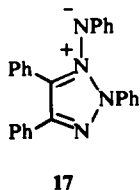
* Spasov et al. (Ref. 23) assigned the 1,2,3,4-dihydrotetrazine structure to 15. It is known that such compounds exist in the open-chain form.

† In a related tetrazole system, evidence has been obtained for photodimerization. Personal communication from Professor R. M. Moriarty, University of Illinois (Chicago).

EXPERIMENTAL

NMR spectra were determined with a Varian A-60 instrument, using TMS as an internal reference. UV spectra were recorded with a Carey Model 14, and IR spectra were obtained for $CHCl_3$ solns with a Perkin-Elmer Model 237 instrument. VPC was carried out with an F and M Model 810, using He as the carrier gas and a thermal conductivity detector. Quantitative VPC analyses utilized appropriate internal standard materials and a calibrated disc integrator.

General photolysis procedure. Except as otherwise noted, solns of the substrates (4–8 mmole) in 100 ml of anhyd THF were placed in cylindrical quartz tubes, purged 1 hr with purified N_2 or argon, and irradiated in a Rayonet chamber reactor using 16 8-W low press Hg lamps (254 mµ, 35°). For substrates bearing Me and cyclopropyl substituents, solns were immersed in a water bath (27°) with the light source, a Hanovia 450 W medium press Hg arc. Runs were stirred magnetically, and evolved N_2 was collected at atm press with a gas buret. Full experimental details for the photolyses of 1 and 2 in THF are reported elsewhere.[1] The same procedures were employed with other solvents.

Preparation and analysis of [15]*N-labelled* 1. 5-Phenyltetrazole [15]N (1 or 4) was prepared from benz-amide-[15]N (Volk Radiochemical Co.) by the method of Herbst.[12b] The ^{15}N enrichment (91%) was determined by photolyzing the tetrazolide anion[1] (all N_2 evolved) and analysing the evolved gas. Analyses were made with a Bendix 3012 time-of-flight mass spectrometer at 70 ev. The procedure of Finnegan *et al.*,[27] using potassium azide-[15]N (95%), was employed to prepare 5-phenyltetrazole-[15]N (1 or 2).

5-Cyclopropyltetrazole (1c). Cyclopropyl cyanide, 13·4 g (0·20 mole), sodium azide, 14·3 g (0·22 mole), ammonium chloride, 3·5 g (0·065 mole) and 100 ml anhyd DMF were stirred and heated at 120–125° for 44 hr. Solvent was removed under reduced press, leaving an almost white paste. The latter was taken up in 50 ml H_2O, acidified with conc HCl (HN_3!) and cooled. The white crystalline ppt was collected, washed with ice water and dried; yield, 12·1 g (55%), m.p. 148–150°. Two additional crystallizations gave the analytical sample, m.p. 149–150°. (Found: C, 43·66; H, 5·49; N, 50·85. Calc. for $C_4H_6N_4$: C, 43·63; H, 5·49; N, 50·88%).

s-Tetrazines by tetrazole photolysis (*Table* 1). After evolution of N_2 had ceased, solvent (THF) was removed under reduced press from the yellow product soln. To remove acidic materials, the residue was dissolved in ca. 30 ml CH_2Cl_2 and extracted twice with 10 ml portions of 5% NaOH aq. The CH_2Cl_2 was evaporated and the residue suspended with 1·0 g $NaNO_2$ in 10 ml 50% aqueous EtOH. The mixture, cooled to 0°, was acidified with 6N H_2SO_4, stirred 15 min and extracted with three 10-ml portions CH_2Cl_2. Evaporation of the dried ($MgSO_4$) soln gave the intensely colored red s-tetrazine products (Table 1). Compounds 8a[28] and 8d[18] were identified by comparison (IR, m.p.) with authentic samples. Compound 8e could not be thoroughly characterized due to its instability. On standing for 15 min at room temp, it loses its red color and is transformed to an amorphous, apparently polymeric material. Structure 8e rests on the method of synthesis, characteristic color, NMR spectrum (vinyl pattern similar to styrene), and IR spectrum (905 cm^{-1})[29] of a freshly prepared sample.

3,6-*Diphenyoxy-s-tetrazine* (8b). Red crystals from MeOH, m.p. 168–169°. (Found: C, 63·09; H, 3·82; N, 21·09. Calc. for $C_{14}H_{10}N_4O_2$=C, 63·15; H, 3·79; N, 21·04%).

3,6-*Dicyclopropyl-s-tetrazine* (8c). Red crystals, purified by alumina chromatography, m.p. 42–44°. (Found: C, 59·29; H, 6·31; N, 34·52. Calc. for $C_8H_{10}N_4$: C, 59·24; H, 6·21; N, 34·55%).

Photolysis of 4-amino-3,5-diphenyl-1,2,4-triazole (11). A soln of 11[3] (3·39 mmole in 100 ml THF) developed a yellow color after 18 hr irradiation at 254 mµ. The solvent was removed under reduced press and the residue suspended in 10 ml toluene. Extraction with three 5-ml portions of 2N NaOH followed by acidification of the extract gave a white ppt (0·580 g, 77%), m.p. 181–188°. The product (3) was purified by dissolving in 2N NaOH, filtering, and reprecipitating by acidification. Purified material melted at 189–190°, as reported for 3,5-diphenyl-1,2,4-triazole.[1] The assignment was confirmed by the IR spectrum.

Photolysis of 5-phenoxytetrazole (1b)—3,5-*Diphenoxy-1,2,4-triazole.* A soln of 1b[30] (10·0 mmole in 120 ml THF) was irradiated (254 mµ) for 54 hr. Solvent was evaporated under reduced press, and the residue was suspended in 40 ml CH_2Cl_2. The suspension was extracted with two 20-ml portions of 5% NaOH and 20 ml water. Following concentration to ca. 20 ml in an air stream, the combined aqueous extracts were acidified with conc HCl, and the resulting suspension was diluted with hot EtOH. On cooling, 0·261 g (21%) of crude, brownish product was obtained, m.p. 159–168°. Three recrystallizations from 70% MeOH gave the analytical sample of 3,5-diphenoxy-1,2,4-triazole, m.p. 179–180°. (Found: C, 66·21; H, 4·41; N, 16·73. Calc. for $C_{14}H_{11}N_3O_2$: C, 66·39; H, 4·38; N, 16·59%).

Phenol (8% by VPC analysis) was found in the initial aqueous filtrate. A 13% yield of 3,5-diphenoxy-1,2,4-triazole, along with 52% of 3,6-diphenoxy-s-tetrazine (**8b**, see above) was isolated from a shorter run (7 hr).

Photolysis of 1,6-dihydro-3,6-dimethyl-s-tetrazine (**12**). Irradiation of a soln of **12**[18] (10·0 mmole, 120 ml THF) for 18 hr gave N₂ (100%) and an almost colorless photolysate. Analysis of an aliquot (VPC, toluene as internal standard) showed the formation of 94% acetonitrile. Another portion (50·0 ml) was evaporated under reduced press to give 0·136 g of an oily white solid, m.p. 72–76°. The m.p. IR and NMR spectra of this material were identical to an authentic sample of **13** prepared by the method of Strain.[31] Treatment of **13** with an acidified soln of 2,4-dinitrophenylhydrazine gave the corresponding hydrazone derivative of acetaldehyde.

Photodecomposition of s-tetrazines. Solns of the tetrazines were irradiated as described above (general photolysis procedure) until the evolution of more than 85% of the N₂ had occurred (48–75 hr). Nitrile products were isolated by preparative VPC and identified by their chromatographic retention times and their IR spectra.

Photolysis of 2,5-diphenyltetrazole (**14**). A soln of 2·26 mmole of **14**[32] in 70 ml THF was irradiated at 254 mμ under N₂. The initially colorless soln developed a deep red-brown color that became light yellow after 20 hr (62 ml gas evolved). Following removal of the solvent, the residue was chromatographed over 25 g of alumina. Elution with hexane-benzene (2:1) gave 0·209 g (63%) of **16**, m.p. 117–119·5°. The identity of **16** was established by comparison (IR, mixed m.p.) with an authentic sample.[33] Further elution with benzene and chloroform gave 0·188 g of colored, non-crystalline materials. A low yield of aniline (< 10%) was detected (VPC) among these products. Photolysis in benzene gave a similar result, 57% of **16**.

A run in THF was interrupted after about 40% of the starting material had photolyzed. Solvent was evaporated and a portion of the residue was analyzed by TLC (silica, benzene-hexane (3:1) solvent), along with standard materials. Spots corresponding to starting material (**14**), triazole (**16**), aniline, and several other products were observed under UV light. A red-brown spot with a migration identical to **15**[23] was present. Alumina column chromatography afforded, in addition to the above-mentioned compounds, a small amount of red-brown material whose IR spectrum agreed with that of **15**.

Photolysis of 1,2-bis-phenylazo-1,2-diphenylethylene (**15**). Irradiation of **15**[23] (as described for **14**, above) gave **16** (83%). The conversion of **15** to **16** was not effected in boiling Ac₂O (60 hr).

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[14] We are indebted to Professor R. M. Moriarty for suggesting these experiments, and for calling the more plausible mechanism to our attention.

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