

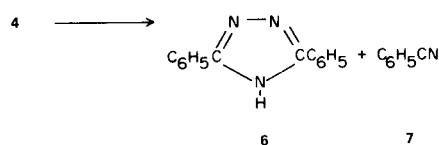
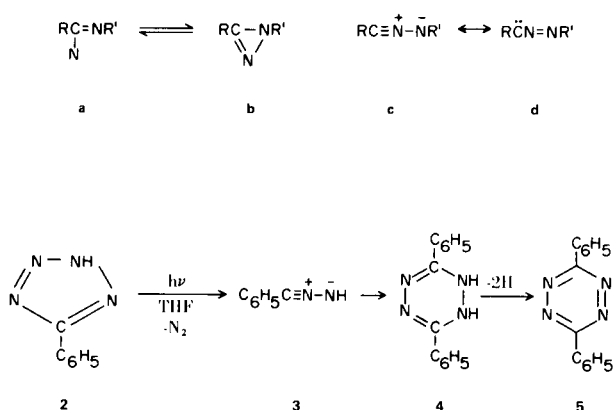
The Azomethine Nitrene. II. Photolysis of 3-Phenyl- $\Delta^2$ -oxadiazol-5-one. (1)

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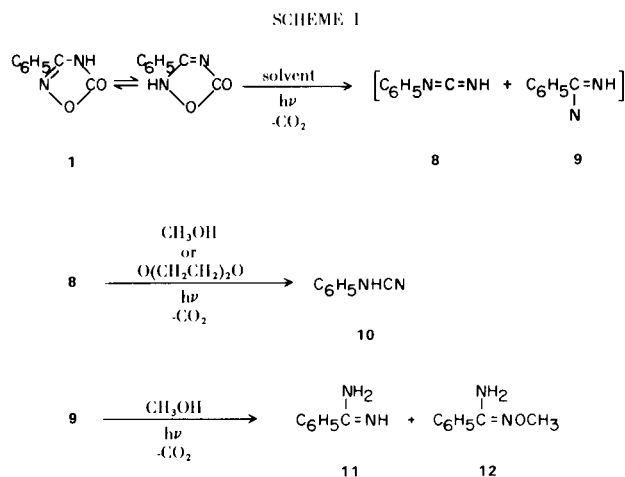
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Irradiation at 2537 Å eliminates carbon dioxide from 3-phenyl- $\Delta^2$ -oxadiazol-5-one in either methanol or dioxane. A migration of phenyl from carbon to nitrogen leads to phenylcarbodiimide (**8**) which tautomerizes into phenylcyanamide (**10**). Benzamidine (**11**) and the *O*-methyl ether (**12**) of benzamidoxime apparently result from hydrogen abstraction and insertion reactions of an intermediate unrearranged azomethine nitrene (**9**). More extensive fragmentation produces benzonitrile (**7**), which is isolated, and presumably phenylcarbene (**20**) to account for benzyl methyl ether (**15**). Generation of the carbene is discussed. The formation of 3,5-diphenyltriazole (**6**), triphenyltriazine (**16**) and *N*-cyanobenzamidine (**15**) remains unexplained.

With and without skeletal rearrangement irradiation at 2537 Å eliminated carbon dioxide from a disubstituted oxadiazolone and also produced more extensive fragmentation (**2**). The present work on the irradiation of 3-phenyl- $\Delta^2$ -oxadiazol-5-one (**1**) was in progress when a report (**3**) appeared on the photochemistry of 5-phenyl-tetrazole (**2**). For the latter reaction the generation of diphenyldihydropyridazine (**4**) from benzonitrilimine (**3**) was assumed (**3**). Oxidation transformed it into diphenyl-tetrazine (**5**) and photo-degradation afforded both 3,5-diphenyltriazole (**6**) and benzonitrile (**7**) (**3,4**). Since benzonitrilimine was neither trapped, *e.g.*, as its adduct with an olefin, nor otherwise detected (**5**), it is now recognized that an alternative formation of (**4**) may have proceeded from the azomethine nitrene (**9**), to be expected from 2-phenyl-1*H*-tetrazole by the elimination of nitrogen. This raises the question of the relationship between an azomethine nitrene **a**, its valence tautomeric azirine **b**, and the resonance hybrid: a nitrilimine **c** ↔ an azocarbene **d**.



In the present work products may be derived from either 3-phenyl- $\Delta^2$ -oxadiazol-5-one or the tautomeric 3-phenyl- $\Delta^3$ -oxadiazol-5-one or a mixture of the two (**6**). Product formation requires both skeletal retention and rearrangement as well as more extensive fragmentation and recombination (Scheme 1).



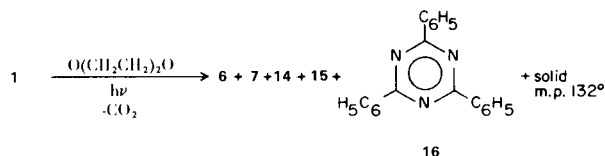
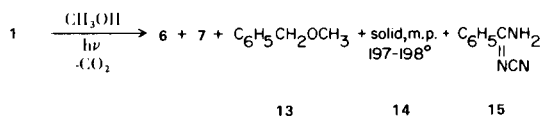
Formation of carbodiimides and their isomerization into cyanamides on irradiation of disubstituted oxadiazolones has been described (**2**). In the present work phenylcarbodiimide (**8**) may have been detected by ir absorption at 2110  $\text{cm}^{-1}$  for the crude product mixture in dioxane. Its expected facile tautomerization permitted the isolation of phenylcyanamide (**10**).

TABLE I  
Separation of Product Concentrate Obtained from Methanol (a)

Compound Number	Fraction I (b)		Fraction II (c)		Fraction III (d)		Yield (f)				
	Gc (e) r.t. Minutes	Yield (f,g) mg.	%	Eluent	Compound Number	Yield (f) mg.	%	Eluent	Compound Number	Yield (f) mg.	%
13 (h)	3.0 (i)	6	1.2	B-C (j), 1:1	10 (k)	15	1.9	B-C (j), 1:4	12 (l)	200	32.5
7 (m)	3.4 (n)	122	18.5 (o)	B-C (j), 1:1 C-E (r), 4:1	6 (p) 15 (s)	tr tr	tr	Ether E-M (t), 20:1	11 (u)	tr (q) tr	tr (q) tr

(a) The concentrate in chloroform solution was extracted first with 10 percent sodium hydroxide, then with 2N hydrochloric acid. (b) Acid and base insoluble oil. (c) After neutralization of this base soluble fraction it was applied to a silica gel column for separation. (d) After neutralization of this acid soluble fraction, extraction with warm hexane-benzene left an insoluble brown crystalline solid. Evaporation of benzene-hexane left a colorless oil which was applied to a silica gel column for separation. The solid, insoluble in hexane-benzene, recrystallized as a trace amount of colorless flakes, m.p. 196-197°, identified by identical ir as 14, also obtained from the reaction in dioxane (Table II). (e) 15% Apiezon on Anakrome, ABS, 80/90, 5 ft. by 0.25 in. Column temperature 125°, pressure 20 psi. (f) Yields are based on the amount (65%) of 1 which reacted. This is assumed to be identical with the yield (65%) of carbon dioxide. (g) As an internal standard, 110 mg. of ethyl benzoate was added. (h) Parent peak m/e 122 (calc'd mw 122), strong m/e 121, 91 (C<sub>7</sub>H<sub>7</sub><sup>+</sup>). The mass spectrum was identical with that for authentic 13. (i) Identical with r.t. for authentic 13. (j) Benzene-chloroform. (k) Initially isolated as an oil with ir absorption identical with that obtained from an authentic sample. After standing for three days the oil completely crystallized to give a solid, m.p. 174-175° after recrystallization from benzene (A. W. Hofmann, *Chem. Ber.*, 18, 3223 (1885) reports a m.p. of 185°. F. Arndt, *Ann. Chem.*, 384, 322 (1911) reported that instead of a simple trimer this is a derivative consisting of two moles of a trimer and one mole of monomer.) Our sample gave ir absorption at 3480 w (NH), 2330 m (C≡N), and 1630 st (C=N) cm<sup>-1</sup>. (l) Colorless crystalline solid, m.p. and mixture m.p. 55-56° (F. Tiemann and P. Krüger, *Chem. Ber.*, 17, 1689 (1884). Ir and nmr absorption were respectively identical with that for an authentic sample. Ir, 1640 cm<sup>-1</sup> str (C=N); nmr (deuteriochloroform), δ 3.83 (s, 3, CH<sub>3</sub>), 4.83 (br, 2, NH<sub>2</sub>), 7.11-7.66 (m, 5, C<sub>6</sub>H<sub>5</sub>). Injection of a pure sample of 12 into the gas chromatograph under the conditions used previously (e) gave two peaks at a r.t. of 3.4 and 36.0 minutes identified with 7 and 12 respectively and with a corresponding peak area ratio of 1:65. (m) Mass spectrum identical with that for authentic 7. (n) Identical with the r.t. for authentic 7. (o) A similar gc separation of the product concentrate before extraction with base and acid gave 37.5% yield of 7. The higher yield can be accounted for by thermal elimination of 7 from 11 (P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, 1966, p. 217.) or its derivative 15, or from 12 (l) during injection. (p) M.p. and mixture m.p. 187-189° (K. I. Potts, *J. Chem. Soc.*, 3461 (1954)). Ir absorption identical with that for an authentic sample. (q) A trace of impure solid gave an ir spectrum closely similar to that for benzamide. Its r.t. R<sub>f</sub> was identical with that for authentic benzamide. (r) Chloroform-ether. (s) M.p. and mixture m.p. with 15 (Table II) 138-139°. Ir absorption identical with 15 (Table II). (t) Ether-methanol. (u) A tentative assignment based on ir absorption (chloroform) of a crude brown oil. Bands at 3540 and 3430 cm<sup>-1</sup> (NH) and 1640 cm<sup>-1</sup> (C=N) are identical with those for authentic benzamide.

Other products:



Strong evidence for the intermediacy of an azomethine nitrene (**9**) is found in benzimidine (**11**) apparently formed as the nitrene, presumably as a triplet, abstracted hydrogen from solvent (7,8). On the other hand an efficient insertion into the OH bond of methanol gave the *O*-methyl ether of benzamidoxime (**12**) and may have proceeded from a singlet azomethine nitrene (7).

Benzonitrile (**7**) represents more extensive fragmentation of **1**. Nitrile formation by similar fragmentations in which the other heterocyclic nitrogen was eliminated as a nitrene was previously observed for disubstituted oxadiazolones (**2**). Although simultaneous formation of imidogen (HN) from **1** may be assumed, it has not been detected. Benzonitrile does not phototrimerize into triphenyltriazine (**16**) (**2,9**), nor is it a 1,3-dipolarophile in the photogeneration of 3,5-diphenyltriazole (**6**) from **1** insofar as

crossover experiments with added acetonitrile or *p*-methoxybenzonitrile did not yield detectable amounts of methyl- or *p*-methoxyphenyl-substituted triazoles. From each reaction only 3,5-diphenyltriazole was obtained. A satisfactory explanation for the formation of the heterocycles **6** and **16** cannot be offered at this time (10). Neither **4** nor **5** are detectably generated from **1** by irradiation.

Phenyl carbene, the apparent precursor for benzyl methyl ether (**13**) by insertion into the OH bond of methanol (11,12), also requires extensive fragmentation of **1** with an apparent tautomeric shift of hydrogen from nitrogen to carbon. An attractive sequence leading to its formation required the intermediacy of 1(*H*)-3-phenyldiazirine (**17**), presumably an antiaromatic ring which rearranges into 3(*H*)-3-phenyldiazirine **18** and/or an azocarbene **19**. Elimination of nitrogen from either of the latter or from tautomeric phenyldiazomethane would leave phenyl carbene. It is assumed that the initial diazirine **17** is in equilibrium with the isomeric azomethine nitrene **9** which may, of course, be formed first. Previously an isomerization

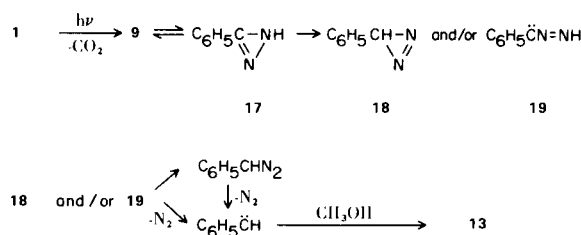


TABLE II

Separation of Product Concentrate Obtained from Dioxane (a)

Fraction I (b)				Fraction II (c)				
Eluent	Compound Number	M.p. °C	Yield (d)		Eluent	Compound Number	M.p. °C	Yield (d)
			mg.	%				
B-C (e), 1:1	<b>10</b> (f)		40	2.0	B-H (g), 4:1	<b>16</b> (h)	226-228	tr
B-C (e), 1:1	<b>6</b> (i)	187-189	30	1.1	B-H (g), 4:1	<b>7</b> (j)		tr
C-E (k), 3:1	<b>15</b> (l)	138-139 (m)	30	1.7	B-H (g), 1:1		132 (n)	tr

(a) The concentrate in chloroform solution was extracted first with 10 percent sodium hydroxide, then with 3*N* hydrochloric acid. (b) After neutralization of this fraction in base it was applied to a silica gel column for separation. (c) Neutralization of this fraction in acid gave a dark tar which recrystallized from ethanol as a trace amount of colorless flakes, m.p. 197-198°, identical with the solid obtained from an ether solution of the product concentrate on cooling and tentatively identified as **11**. (d) Yields are based on the amount (95%) of **1** which reacted. This is assumed to be identical with the yield (95%) of carbon dioxide. (e) Benzene-chloroform. (f) See Table I (k). (g) Benzene-hexane. (h) Ir identical with that from an authentic sample. Mixture m.p. showed no depression. (i) Identified by a mixture m.p., ir and the *R<sub>f</sub>* identical with similar values for authentic material. (j) Identified by ir. (k) Chloroform-ether. (l) Ir absorption occurred at 3420 m (NH), 2200 st (C≡N), 1650 st (C=N) cm<sup>-1</sup> and mass spectrometric peaks were observed at M<sup>+</sup> 145; M - NH<sub>2</sub>, 129; M - HCN, 118; m/e 103, C<sub>6</sub>H<sub>5</sub>CN; m/e 91, C<sub>6</sub>H<sub>5</sub>N; m/e 77, C<sub>6</sub>H<sub>5</sub>. (m) Ref. 13 reports m.p. 142°. (n) A colorless solid recrystallized from benzene-hexane. Ir absorption occurred at 3450 m (NH) cm<sup>-1</sup> and M<sup>+</sup> 324 was observed in the mass spectrometer. It has not been identified.

of an *N*-alkyl azomethine nitrene **a**  $\rightleftharpoons$  azirine **b** into a nitrilimine **c**  $\leftrightarrow$  an azocarbene **d** could not be detected (2). Insofar as **3** and **19** represent the same resonance hybrid while **3** and **17** are valence isomers, it would be of interest to investigate the formation of the ether **13** from phenyl-tetrazole (**2**) by irradiation in methanol.

From a partial analysis of the structure of **14**, obtained in trace amount, NH and C=N bonds were detected by characteristic ir absorption and *m/e* at 238 was observed. *N*-Cyanobenzamidine (**15**) (13), was also obtained in trace quantity.

#### EXPERIMENTAL

Solvents were purified and deoxygenated (2). Irradiation was conducted in a Rayonet Unit with 16 low pressure lamps emitting 2537 Å. According to a general procedure (2) irradiation of 1.0 g. (6.1 mmoles) of 3-phenyl- $\Delta^2$ -oxadiazol-5-one, m.p. 197-198° (prepared according to Falck (14) for 7 hours in 500 ml. of methanol released 65% of the theoretical amount of carbon dioxide, and for 20 hours in 500 ml. of dioxane released 95% of the theoretical amount of carbon dioxide.

Prior to column chromatographic separation, volatile components were separated by gc (see Table I (o) for gc separation of product concentrate in methanol). As an internal standard, 94 mg. of benzyl alcohol was added to the product concentrate obtained from the reaction in dioxane. Separation by gc gave 500 mg., 41%, (see Table I (f)) of benzonitrile (**7**) with a rate of 3.4 minutes identical with that for an authentic sample. Probably thermolysis, during injection into the gc, of **11** (Table I (o)) and **15** partially accounts for **7**.

On cooling in the refrigerator an ether solution of the dioxane product concentrate, a solid **11** separated as colorless flakes; m.p. 197-198°; 30 mg., 1.0%; ir absorption ( $\text{cm}^{-1}$ ): 3550 st, 3440 st ( $\text{NH}_2$ ), 1640 st (C=N) and mass spectra:  $M^+$  238;  $M - \text{NH}_2$ , 222; 208, metastable; 193;  $M - \text{C}_6\text{H}_5$ , 161; 146;  $M - \text{C}_6\text{H}_5\text{CN}$ , 135; 118; 104; 103; 91; 77. It was also found in the acid soluble fraction (Table II).

Irradiation of Phenylloxadiazolone in the Presence of Acetonitrile and *p*-Methoxybenzonitrile.

Following the general procedure (2), a solution of 1.0 g. (6.1 mmoles) of phenylloxadiazolone (**1**) in 250 ml. of dioxane and 16 g. (120.0 mmoles) of *p*-methoxybenzonitrile was irradiated under nitrogen at 2537 Å for 20 hours as 90% of the theoretical amount of carbon dioxide was collected as 1.10 g. (5.5 mmoles) of barium carbonate. When 1.0 g. (6.1 mmoles) of **1** in 500 ml. of acetonitrile was treated similarly, 82 percent of the theoretical amount of carbon dioxide was obtained. Each reaction mixture was worked-up in the manner previously discussed for the isolation of triazoles (2). From each reaction mixture only 3,5-diphenyltriazole (**6**) could be detected in 10 and 15 mg. (about one percent)

amounts, respectively. It was identified by direct comparison with an authentic sample. Neither *p*-methoxyphenyl- nor methyl-substituted triazoles could be detected. Authentic 3-*p*-methoxyphenyl-5-phenyl-1,2,4-triazole and 3-methyl-5-phenyl-1,2,4-triazole were prepared. By tlc separation of each of the above crude irradiation product mixtures no material was found to possess the same  $R_f$  value as that observed for these authentic triazoles.

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- (2) J. H. Boyer and P. J. A. Frints, *J. Heterocyclic Chem.*, **7**, 59 (1970).
- (3) P. Scheiner, *J. Org. Chem.*, **34**, 199 (1969).
- (4) R. Huisgen, J. Sauer and M. Seidel, *Ann. Chem.*, **645**, 146 (1962).
- (5) Trapping intermediate diphenylnitrilimine obtained by irradiating 2,5-diphenyltetrazole with dimethyl fumarate and with dicyclopentadiene was reported (3) as inferential support for **3**.
- (6) The preparation and photochemistry of  $\Delta^3$ -oxadiazolones is underway.
- (7) D. S. Breslow, M. F. Sloan, N. R. Newburg and W. B. Renfrow, *J. Am. Chem. Soc.*, **91**, 2273 (1969) conclude that certain insertions are nitrene singlet reactions and hydrogen abstraction is a nitrene triplet reaction.
- (8) H. Newman, *Tetrahedron Letters*, 2417 (1968) reports the formation of benzoylbenzamide by hydrogen abstraction from ether by an intermediate, which may be represented as an azomethine nitrene,  $\text{C}_6\text{H}_5\text{C}(\text{N})=\text{N}-\text{COC}_6\text{H}_5$ , produced from 3,5-diphenyl-1,2,4-oxadiazole by irradiation.
- (9) H. Newman (8) reports that irradiation of benzonitrile does not produce **16** and the nitrile may be recovered. This has been confirmed. H. N. suggests that an excited state of benzonitrile, on formation by dissociation of 3,5-diphenyl-1,2,4-oxadiazole, trimerizes into **16**.
- (10) Trimerization with dehydrogenation of benzaldimine leads to the triazine **16** as a competing reaction leads to triphenylimidazole (**2**). Since the latter is not a detected product from the irradiation of **1** it is doubtful that benzaldimine is produced as an intermediate.
- (11) D. Bethell and D. Whittaker, *J. Chem. Soc., B*, 778 (1966).
- (12) Irradiation of methanolic solutions of an equimolar mixture of 5-phenyltetrazole and sodium methoxide gave nearly quantitative conversion to benzyl methyl ether. Phenyl carbene was an assumed intermediate (3).
- (13) J. Goerdeler and D. Loevenich, *Chem. Ber.*, **86**, 890 (1953).
- (14) E. Falck, *ibid.*, **18**, 2467 (1885).

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