

The Azomethine Nitrene. I. Pyrolysis and Photolysis of Δ^2 1,2,4-Oxadiazoline-5-ones (I)

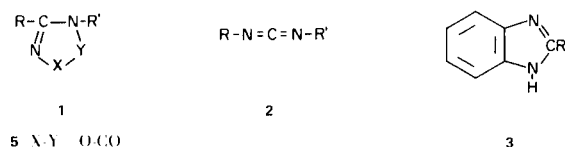
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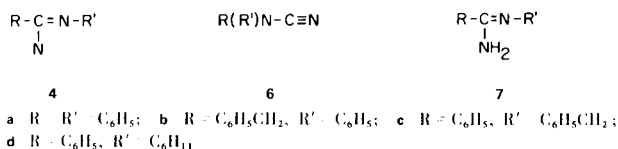
Both photolytic and pyrolytic fragmentation of the oxadiazolone ring produces carbon dioxide and a residue which may exist in part as an intermediate azomethine nitrene and may react with or without rearrangement and/or further fragmentation. Rearrangement produces carbodiimides **2** and cyanamides **6**. Thermal and photo-isomerization of carbodiimides into cyanamides provides a key step in an explanation for the formation of the latter from an oxadiazolone. A highly selective cyclization produces a benzimidazole **3** when a suitable aryl substituent is at nitrogen. The formation of *N*-phenylbenzimidine **7a** from 3-phenyl-4-benzyloxadiazolone **5c** requires a 1,4-migration from carbon to nitrogen followed by hydrolysis. The same or similar migration of hydrogen and subsequent ring-closure with dehydrogenation provides the formation of 2-phenylquinazoline **8**. Products which require no rearrangement of the residue include amidines **7** and triazoles **10**. A portion of each triazole corresponds to a nitrile, in turn a product along with a simple nitrene, of more extensive fragmentation of the oxadiazolone ring. Phenyl, benzyl, and cyclohexyl nitrenes are respectively detected by the isolation of aniline, benzaldehyde and cyclohexanone. Other recombination reactions bring about the formation of triphenyltriazine **13** and triphenylimidazole **14**.

Introduction.

The loss of X-Y, e.g., O-CO (2,3), O-SO (3,4), N₂ (5,6,7) from a five-membered aromatic heterocycle **1** leaves a residue generally isolated in a rearranged form such as a carbodiimide **2** and/or a benzimidazole **3** when R' is a suitable group, e.g., phenyl. No product other than **2** or **3** isomeric with an azomethine nitrene **4**, often an assumed intermediate, has been previously reported (2).



5 X-Y O.CO



In principle the presence of a nitrene may be demonstrated by its addition to an unsaturated linkage, hydrogen abstraction and/or intermolecular insertion into a CH bond (8). This work was undertaken [1] to find products, if present, from these reactions of azomethine nitrenes possibly generated by pyrolytic and photolytic fragmentation

of an oxadiazolone **5**, and [2] to investigate the fate of an intermediate [a] which must choose between intramolecular cyclizations into two different five-membered aromatic rings, [b] from which the only available intramolecular cyclization affords a six-membered dihydroaromatic ring and [c] from which intramolecular cyclization, should it occur, requires attack at a paraffinic CH bond.

Results.

By treating appropriate amidoximes with ethyl chloroformate, oxadiazolones **5a, b, c, d** were readily obtained. When each was heated about 250° or irradiated at 2537Å, carbon dioxide was smoothly ejected. The residue underwent reactions with and without rearrangement and/or further fragmentation. Products are recorded in the accompanying Scheme I and in Table II.

Rearrangement products include carbodiimides **2**, cyanamides **6** and 2-substituted benzimidazoles **3**. From each of four oxadiazolones, photolysis gave the appropriate isomers **2** and **6** in combined yields of less than five percent. From the four oxadiazolones investigated under pyrolysis conditions, carbodiimides and cyanamides, with the following exception, were not detected in any product mixture. Phenylbenzylcyanamide was produced in trace amount from 3-benzyl-4-phenyloxadiazolone **5b** by pyrolysis but could not be detected in the product mixture obtained by the pyrolysis of the isomeric 3-phenyl-4-benzyloxadiazolone **5c**. When there is a suitable 4-aryl

TABLE I

Diphenylcarbodiimide **2a** and 2-Phenylbenzimidazole **3a** from Diphenyldiazoles **1**, R=R'=C₆H₅

Starting Material 1 X-Y	Temp. °C	Pyrolysis			Ref.	Solvent	Photolysis < 3000 Å		Ref.
		% Yield 2a	% Yield 3a	% Yield 2a			% Yield 3a		
O-CO	260	0	90	2a	Dioxane	2	86		
N ₂	200	76	23	5	Benzene	0	66	3,6,7	
O-SO	100	100	0	4	Ethyl acetate	62	3	3,10	

TABLE II

Photolysis of Oxadiazolones (**5**)

No.	Amt. g. (mmole)	Dioxane ml. (Time, hr.)	Products, Yield % (a)							
			CO ₂	2 and/ or 6	3 or 8	7	10	RCN R	13	Other
a	1.19 (5)	500 (11)	quant.	1.9 (b)	86 (c)	--	--	C ₆ H ₅ trace		C ₆ H ₅ NH ₂ 4
b	1.26 (5)	150 (19)	58.6 (d)	4 (e)	64 (f)	4.7	--	C ₆ H ₅ CH ₂ 6.7		C ₆ H ₅ NH ₂ trace
c	1.26 (5)	500 (15)	98.2 (g)	2.4 (e)	1 (h)	a 20.2 c --- (i)	c 2 c' 1	C ₆ H ₅ 5.4	2.2 (j)	C ₆ H ₅ CHO 7.5
d	2.44 (10)	1000 (18)	92.5 (k)	1.7 (l) 0.6	-- (m)	19.6 (n)	d 9.3	C ₆ H ₅ 7.2	0.9	(CH ₂) ₅ CO 9.9 (o)

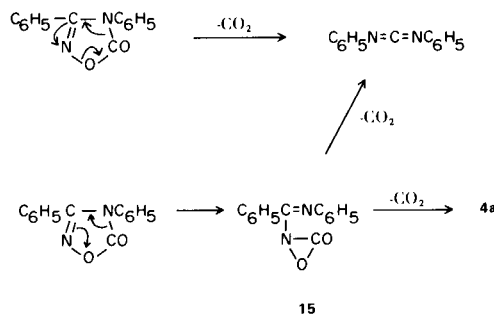
(a) Except for carbon dioxide yields are based on recovered **5**. Aldehydes and ketones are produced by hydrolysis of corresponding photo-products. (b) **2a** isolated as *N,N'*-diphenylurea, m.p. 237-238° (C. Graebe and S. Rostovzeff, *Chem. Ber.*, **35**, 2750 (1902)) by elution with ethylacetate. (c) 2-Phenylbenzimidazole **3a**. (d) Starting material recovered in 42%. (e) Phenylbenzylcyanamide **6b** (≡ **6c**). A trace of **2b**, obtained from **5b**, was detected by tlc and by ir absorption. (f) 2-Benzylbenzimidazole. (g) Starting material recovered in 2.4%. (h) 2-Phenylquinazoline. (i) There was no trace of *N*-benzylbenzamidine, **7c**. *N*-phenylbenzamidine **7a** was isolated in 20.2% yield including benzanilide, 4.5%, produced by partial hydrolysis. (j) *Anal.* Calcd. for C₂₁H₁₅N₃: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.65; H, 4.96; N, 13.69. (k) Starting material was recovered (6.2%). (l) *N*-cyclohexyl-*N'*-phenylurea, m.p. 181-182° (A. Skita and H. Rolfes, *Chem. Ber.*, **53**, 1248 (1920)), 37 mg., 1.7%, is assumed to be the hydrolysis product from *N*-cyclohexyl-*N'*-phenylcarbodiimide **2d**. The cyanamide **6d** was obtained in 0.6% yield. (m) There was no conclusive evidence for the formation of 2-phenyl-4,5,6,7,8,9-hexahydrobenzimidazole. F. Winternitz, M. Mousseron and R. Dennilaule, *Bull. Soc. Chim. France*, 382 (1956), reports the *trans* modification, m.p. 180° (n) *N*-cyclohexylbenzamide, m.p. 148-149° (33), 24 mg., 1.3% and benzamide, m.p. 125-126°, 23 mg., 2%, are assumed to be hydrolysis products from **7d** and are included in the yield of 19.6%. Also included in the yield for **7d** is its adduct **9** with *N*-cyclohexyl-*N'*-phenylcarbodiimide **2d**. The hydrochloride, 47 mg., m.p. 260-261°, of the guanidine **9** recrystallized from ethanol-hexane as a colorless solid (a Lassaigne test for chlorine was positive). *Anal.* Calcd. for C₂₆H₃₅N₄Cl: C, 71.12; H, 8.03; N, 12.76; mw 439. Found: C, 70.64; H, 8.00; N, 12.77; m/e 402 (100). The strong molecular ion is consistent with C₂₆H₃₄N₄ and represents the loss of hydrogen chloride. A similar absence of the representation of hydrogen chloride in the molecular ion obtained by mass spectrometric analysis of an amine hydrochloride was reported by A. Tatematsu, T. Goto, T. Nakamura, and S. Yamaguchi, *J. Pharm. Soc. Japan*, **86**, 195 (1966). Other peaks at 404 (4), 403 (28), 401 (79) reflect not only the absence of chlorine in the molecular ion but also the presence of a strong M-1 peak. The guanidine hydrochloride was identical with a sample independently prepared from the carbodiimide **2d** and the amidine **7d** in hydrochloric acid. (o) A trace of benzaldehyde is unaccounted for.

TABLE III
Photorearrangement of Carbodimides $RN=C=NR'$ into Cyanamides $RR'NCN$

R R'	RN=C=NR' Properties		Reaction Data (a)			RR'NCN Properties			
	Uv (b) $m\mu$ ($\times 10^{-3}$)	Nmr δ (CCl_4)	G.c.r.t. min. (aa) B.p. °C (mm.)	conc. m/l irr. time	Urea (c) Yield % M.p. °C	RR'NCN Yield % (d)	Uv (b) $m\mu$ ($\times 10^{-3}$)	Nmr δ (CCl_4)	G.c.r.t. min. (aa) M.p. °C
C_6H_5 C_6H_5	202 (60) 242 (26) 275 (9.2) 283 (7.3)	7.40- 6.85 m, C_6H_5	6.5 150 (4) (c)	0.009 36 hours	82 236- 238 (f)	0 (e)	199 (34.6) 218 (9.3) 236 (12.1) 255 (11.9) 276 (2.3) 283 (1.4)	7.60- 6.93 m, C_6H_5	6.5 70-71 (h)
C_6H_5 $C_6H_5CH_2$	194 (29) 202 (20) 251 (11) 277 (4.1) 284 (3.1)	7.33 6.80 m, 10, C_6H_5 4.31 s, 2, CH_2	6.0 145 (0.5) (i)	0.033 36 hours	2.6 167- 168 (j)	13.8 (k)	197 (69) 234 (17.6) 273 (2.1) 281 (1.9)	7.43-6.88 m, 10, C_6H_5 4.61 s, 2, CH_2	7.5 59-60 (l)
C_6H_5 (m) CH_3	193 (32.6) 203 (24.5) 249 (10.7) 278 (3.2) 286 (2.1)	7.40-6.80 m, 5, C_6H_5 3.03 s, 3, CH_3	1.2 (cc) 50 (1) (n)	0.100 80 hours	33 147 (o)	2.0 (p)	197 (30.0) 233 (15.0) 273 (1.3) 282 (1.2)	7.50-6.80 m, 5, C_6H_5 3.23 s, 3, CH_3	2.2 (cc) 26-27 (q)
C_6H_{11} C_6H_{11}	188 (4.9) 205 (0.16)	3.15 br, 2NCH- 2.15-1.00 m, 20, CH_2	7.0 -- (r)	0.18 1 week	92 227 229 (s)	11.0 (t)	194 (0.65)	2.71 br, 2, NCH 2.15-0.88 m, 20, CH_2	11.0 (bb) 44.45 (u)
C_6H_5 C_6H_{11}	192 (31) 202 (24.2) 215 249 (11.5) 278 (3.4) 286 (2.3)	7.42-6.68 m, 5, C_6H_5 3.35 br, 1, NCH 2.10-0.82 m, 10, CH_2	3.4 130 (1.3) (v)	0.10 24 hours	66 182- 183 (w)	14.6	196 (27.7) 202 (26.6) 221 (7.2) 248 (18.3) 275 (3.3)	7.48-6.81 m, 5, C_6H_5 3.52 br, 1, NCH 2.16-0.86 m, 10, CH_2	5.7 -- (x)

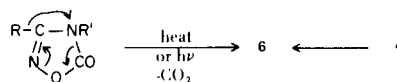
(a) Each reaction was run in dioxane freshly distilled from lithium aluminum hydride. (b) Uv data obtained from *n*-hexane solutions in a Cary 14 spectrophotometer. With water as the reference, hexane has an absorbance of 0.05 at 230 $m\mu$ increasing to 0.55 at 200 $m\mu$ and over 1.0 at 190 $m\mu$. (c) Carbodiimide remaining after irradiation was quantitatively converted into a urea by treatment with 3*N* hydrochloric acid at 25° for 0.5 hour. (d) Based on each unreacted carbodiimide recovered as its urea derivative. The cyanamides were unreactive to the acid treatment. (e) R. Stolle, *Chem. Ber.*, **41**, 1125 (1908), reported b.p. 163-165° (11 mm.). After one week a sample had appreciably solidified, presumably a result of reversible trimerization (ref. 51). (f) C. Graebe and Rostovtzeff, *Chem. Ber.*, **35**, 2750 (1902), reported m.p. 238-239° (g) Irradiation for 12 hours extensively decomposed diphenylcyanamide in dioxane, leaving a dark-brown to black solution. (h) Ref. 46. (i) Ref. 42 reported 148-152° (2.5 mm.). (j) H. Ley and P. Krafft, *Chem. Ber.*, **40**, 703 (1907). (k) A yellow-brown intractable oil was the major product. (l) J. von Braun and R. Schwarz, *Chem. Ber.*, **35**, 1284 (1902). (m) *Anal. Calcd.* for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.75; H, 6.01; N, 21.22. On standing, polymerization produced a solid. E. Hakuri, I. Inaiki and E. Imoto, *Bull. Chem. Soc. Japan*, **38**, 1806 (1965), reported a preparation for *N*-chloro-*N'*-phenylacetamide and silver oxide but gave no physical properties. (n) K. Hartke and J. Bartulin, *Angew. Chem.*, **74**, 214 (1962), reported polymerization prevented distillation. (o) O. Degner and H. von Pechman, *Chem. Ber.*, **30**, 650 (1897), reported m.p. 149-150°. (p) Dark-brown insoluble material m.p. > 250° was the major product. (q) O. Wallach, *Chem. Ber.*, **32**, 1873 (1899). (r) M.p. 32-33°. Ref. 45 reported m.p. 35-36°. (s) A. Skita and M. Rolles, *Chem. Ber.*, **53**, 1248 (1920). (t) The major product was an unidentified yellow-brown oil. Irradiation of *N,N'*-dicyclohexylcarbodiimide by a high-pressure Hanovia immersion lamp (100 w) for 7 hours produced *N,N'*-dicyclohexylcyanamide in nearly the same yield. (u) Ref. 48 reported m.p. 45-47°. (v) Ref. 44 reported b.p. 116-120° (0.35 mm.). (w) Ref. (s) p. 1242. (x) See preparation of this new compound. (aa) Column temperature 200° except where noted. (bb) Column temperature 165°. (cc) Column temperature 182°.

of detecting an isomeric Δ^3 -oxadiazolone prior to complete loss of carbon dioxide from a Δ^3 -oxadiazolone **5**, it is considered unlikely that a ketoazirane **15** may be an intermediate with an appreciable lifetime. If formed, it apparently loses carbon dioxide more rapidly than it isomerizes. The Δ^3 -oxadiazolones are now being investigated.



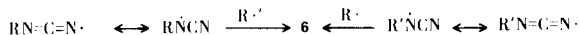
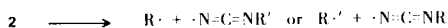
Irradiation of diphenyloxadiazolone in dioxane, photosensitized by *m*-methoxyacetophenone at 3000Å or by benzophenone at 3500Å, did not produce detectable amounts of either diphenylcarbodiimide or diphenylcyanamide. On the other hand, irradiation at 2537Å of the same oxadiazolone in dioxane containing piperylene, a triplet quencher, raised the yield of diphenylcarbodiimide from two to five percent (12). Failure to detect diphenylcyanamide may be attributed to photo-degradation (9). These results tend to support the formation of a carbodiimide from an excited singlet state (12). For reasons outlined above, it is preferred to identify this with an oxadiazolone, or perhaps with a ring-opened isomer, rather than with an intermediate azomethine nitrene.

Isomerization of five carbodiimides by irradiation (Table III) and one by heating has been independently established to give cyanamides **6**. This provides a key step for a possible formation of the latter from oxadiazolones **5**, but it does not preclude a rearrangement concerted with elimination of carbon dioxide. No detectable response to either triplet photosensitization or quenching of oxadiazolones, though indecisive, suggests that cyanamides are not being produced from azomethine nitrenes. Isomerization of a carbodiimide cannot proceed from a singlet or triplet nitrene since known reactions of such an intermediate are not detected (*vide infra*). Conceivably cyanamide



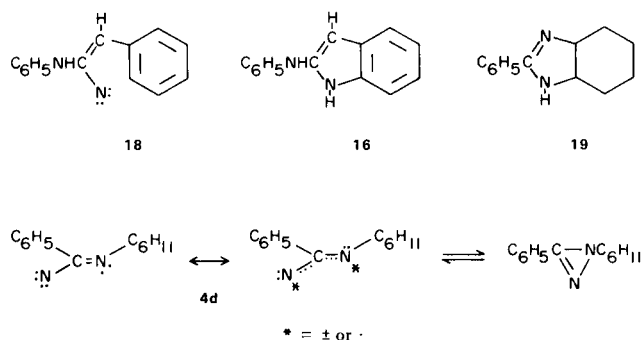
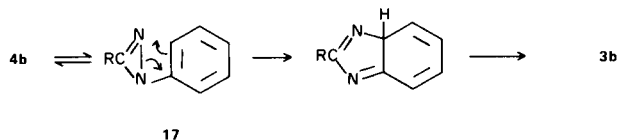
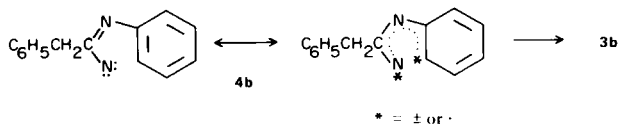
formation from a carbodiimide may result from either bond-cleavage and radical recombination within the solvent cage or an intramolecular cyclic reorganization of σ and π electrons. Either process may account for the apparent

absence of formation of R_2 , R_2' , $(RNCN)_2$, $(R_2'NCN)_2$, R_2NCN and $R_2'NCN$ and is not inconsistent with the failure of irradiation in the presence of acetophenone to reveal a photosensitization effect.



Cyclization to form a benzimidazole **3** and intermolecular hydrogen abstraction to form an amidine **7**, heretofore undetected, appear to proceed from an azomethine nitrene by its appropriate reaction with a CH bond. The cyclization requires either [1] initial opening of an oxadiazolone ring followed by a ring-closure which is either sequential or concerted with separation of carbon dioxide or [2] initial expulsion of carbon dioxide by concerted cleavage of two bonds followed by cyclization. An azomethine nitrene **4** is generated by path [1] if carbon dioxide elimination occurs more rapidly than other reactions of an initial ring-opened diradical or ketoazirane **15** and is produced directly by path [2].

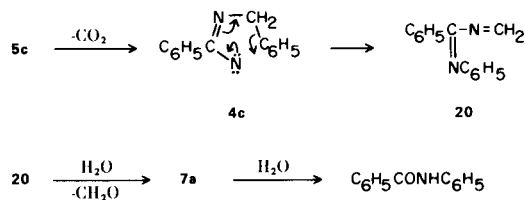
In the pyrolytic and photolytic fragmentation of 3-benzyl-4-phenyloxadiazolone **5b** an intermediate was highly selective in undergoing a cyclization leading to 2-benzylbenzimidazole **3b** rather than to 2-anilinoindole **16** which was not detected. This discrimination between two possible ring-closures may be attributed to an electron delocalization in an intermediate azomethine nitrene **4b** or to ring-expansion of an intermediate diazirine **17** (13, 14a), either of which would assist imidazole ring formation. A similar assistance to indole ring formation is unavailable in the absence of a prior tautomerism into a vinyl nitrene **18**.

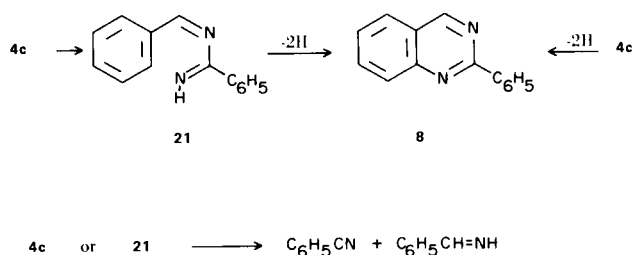


Lack of evidence for the presence of 2-phenylhexahydrobenzimidazole **19** from the pyrolysis or photolysis of 3-phenyl-4-cyclohexyloxadiazolone **5d** was not unexpected. In this instance cyclization may be inhibited by a preferred *syn* configuration of the intermediate **4d**. This configuration is expected if the electrostatic attraction between the lone pair of electrons and the azomethine nitrogen is sufficient. Such attraction may, of course, result in ring-closure to form an intermediate diazirine.

Neither intramolecular nor intermolecular insertion into a CH bond could be detected. On the other hand intermolecular hydrogen abstraction is required for the formation of certain amidines **7**, each in low yield, from the corresponding oxadiazolone by either pyrolysis or photolysis. The tentative assignment that hydrogen abstraction proceeds from a triplet (8) azomethine nitrene **4** is supported by work to be reported on sensitized photolysis of oxadiazolones.

A 1,4-migration by either phenyl or hydrogen in an intermediate generated from 3-phenyl-4-benzoyloxadiazolone **5c** may be either concerted with or subsequent to the loss of carbon dioxide after ring opening and brings about the formation of the corresponding unisolated imines **20** and/or **21**. When loss of carbon dioxide is faster, the rearrangements may proceed predominantly from the nitrene **4c** (14b,15). Assuming that the formation of 2-phenylquinazoline **8** requires cyclization from either the nitrene **4c** (16) or the imines **20** and/or **21**, it apparently competes poorly with further dissociation into benznitrile and benzaldimine. The latter is a known precursor for triphenyltriazine **13** and triphenylimidazole **14** (17).





Hydrolysis during work-up produces benzanilide from **7a** (also isolated) and benzaldehyde from either **21** or benzaldimine (both unisolated). Further investigation on this new rearrangement and on the formation of triazoles is planned.

EXPERIMENTAL

Amidoximes and Oxadiazolones.

With minor modifications of known preparation, *N*-phenylbenzamidoxime, m.p. 134-135° (**18**), *N*-benzylbenzamidoxime, m.p. 112-114° (**19**), 3,4-diphenyloxadiazolone **5a**, m.p. 166-167° (**2**), and 3-phenyl-4-benzyloxadiazolone **5c**, m.p. 84.5-85° (**20**) were obtained.

N-Cyclohexylbenzamidoxime.

During 15 minutes a colorless solution of benzonitrile oxide in 200 ml. of ether, prepared from 15.5 g. (0.01 mole) of benzoylchloride oxime (**21**) was slowly dropped into 99.0 g. (1 mole) of well-stirred cyclohexylamine and the colorless solution was stirred for an additional 24 hours at room temperature. After removal of ether in a rotary evaporator, excess cyclohexylamine was removed *in vacuo* at the water aspirator and the last traces were removed from the remaining syrup at 0.5 mm., while the temperature of the distilling flask was maintained at 60-70°. Cooling a pale yellow syrup residue mixed with 25 ml. of hexane in an ice-bath gave a colorless solid which recrystallized from hexane as colorless prisms, 13.5 g. (0.062 mole), 62%, of *N*-cyclohexylbenzamidoxime, m.p. 97-98°.

Anal. Calcd. for $C_{13}H_{18}N_2O$: C, 71.53; H, 8.31; N, 12.83. Found: C, 71.50; H, 8.31; N, 12.78.

N, α -Diphenylacetamidoxime.

This compound was prepared at room temperature in better yield than had been reported for the preparation (**22**) in boiling aqueous solution. To a stirred colorless solution of 10.2 g. (0.15 mole) of hydroxylamine hydrochloride in 90 ml. of water, an emulsion of 21 g. (0.1 mole) of *N*, α -diphenylacetamidine (**23**) in 90 ml. of ethanol was added at room temperature. After a few minutes the amidine hydrochloride had dissolved completely and after 15 minutes a colorless precipitate appeared. Stirring was continued for 2 hours and the colorless crystals of *N*, α -diphenylacetamidoxime were isolated, 5.5 g. (0.0243 mole), 24.3%, colorless needles, m.p. 140-141°. The pale yellow filtrate was basified with ammonia and ethanol was removed in a rotary evaporator. After cooling in an ice-bath, colorless *N*, α -diphenylacetamidoxime, 7.0 g. (0.0309 mole) 30.9%, m.p. 137-139°, was isolated and recrystallized from ethanol as colorless needles, m.p. 140-141°. Extraction of the water layer with ether gave a dark brown oil, from which no more amidoxime was obtained.

3-Phenyl-4-cyclohexyloxadiazolone (**5d**).

To a stirred solution of 21.8 g. (0.1 mole) of *N*-cyclohexylbenzamidoxime in 300 ml. of toluene and 30 ml. of pyridine in a 500 ml. round bottomed flask, 10.8 g. (0.1 mole) of ethyl chloroformate was added dropwise. While the addition progressed, a colorless precipitate of hydrochloride salts formed. When all of the ethyl chloroformate was added, the flask was fitted with a heating mantle and condenser, and the reaction mixture was refluxed for 30 minutes, during which time the solution turned pale brown. After removal of the solvents (in a rotary evaporator) a pale brown syrup was left, to which 200 ml. of chloroform was added and the resulting mixture was extracted with 2*N* hydrochloric acid, washed with water, dried over magnesium sulfate and the chloroform solution applied to a chromatographic column containing 60 g. of dry aluminum oxide. On elution with chloroform, colorless crystals of 3-phenyl-4-cyclohexyl-1,2,4-oxadiazol-5-one, 21.0 g. (0.086 mole) 86%, m.p. 116-117° was obtained. Recrystallization from benzene-hexane (1:3) gave colorless flakes, m.p. 117-118°. Nmr (deuteriochloroform) δ 7.70-7.20 (m, 5 aromatic H), 3.60 (bubble, 1, CH), 2.36-0.80 (m, 10, CH₂); $\mu\nu$ max (hexane) in μ (ϵ) 197 (24,000), 208 (12,000), 217 (9,700), 240 (4,000); ir (chloroform) 1780 cm^{-1} (C=O).

Anal. Calcd. for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.46. Found: C, 68.76; H, 6.70; N, 11.34.

3-Benzyl-4-phenyloxadiazolone (**5b**).

This compound was prepared in similar manner from 22.6 g. (0.1 mole) of *N*, α -diphenylacetamidoxime and 10.8 g. (0.1 mole) of ethyl chloroformate. After chloroform elution from an alumina column, colorless crystals, m.p. 76-78°, 22 g., 87%, recrystallized from hexane-benzene (3:1) as colorless needles, m.p. 78-79°. Nmr (deuteriochloroform) δ 7.50-6.75 (m, 10, aromatic H) 3.75 (s, 2, CH₂); $\mu\nu$ max (hexane) in μ (ϵ) 197 (25,600), 225 (6,000), 251 (380); ir (chloroform) 1780 cm^{-1} (C=O).

Anal. Calcd. for $C_{15}H_{12}N_2O_2$: C, 71.42; H, 4.79; N, 11.10. Found: C, 72.09; H, 4.80; N, 11.32.

The following compounds, needed for confirmation of products, were prepared by known methods: 2-phenylbenzimidazole m.p. 290-291° (**2**); 2-benzylbenzimidazole m.p. 185-187° (**24**); *N*-phenylbenzamidine (**7a**) m.p. 114-115° (**22**); *N*, α -diphenylacetamidine (**7b**) m.p. 138-139°; *N*-benzylbenzamidine (**7c**) m.p. 74-75° (**25**); *N*-cyclohexylbenzamidine (**7d**) m.p. 114-115° (**26**); 2-phenylquinazoline (**8**) m.p. 99-100°, picrate m.p. 162-163° (**27**); 3,5-diphenyl-1,2,4-triazole (**10c**) m.p. 189-190° (**28**); 3,4,5-triphenyl-1,2,4-triazole (**10c'**) m.p. 294-295° (**29**); 2,4,6-triphenyl-1,3,5-triazine (**13**) m.p. 231-232° (**30**); 2,4,5-triphenylimidazole (**14**) m.p. 274-275° (**31**); 2-phenylacetamide, m.p. 154-155° (**32**); *N*-cyclohexylbenzamide, m.p. 148-149° (**33**); diphenylcarbodiimide b.p. 148-150° (4 mm.) (**34**); benzylphenylcarbodiimide b.p. 143-145° (0.5 mm.) (**35**); cyclohexylphenylcarbodiimide b.p. 128-130° (1.3 mm.) (**36**); diphenylcyanamide m.p. 70-71° (**37**); and benzylphenylcyanamide m.p. 59-60° (**38**). An independent preparation of 1-cyclohexyl-3,5-diphenyltriazole m.p. 106-107° will be published elsewhere.

1,4-Diphenyl-5-cyclohexyl-2-cyclohexylamino-1,3,5-triaz-1,3-pentadiene (**9**).

A mixture of 0.20 g. (1.0 mmole) of *N*-cyclohexyl-*N'*-phenylcarbodiimide (**2d**) (**39**) and 0.202 g. (1.0 mmole) of *N*-cyclohexylbenzamidine (**7d**) (**26**) in 5 ml. of dioxane was stored three days at room temperature. Removal of dioxane left an oil which slowly crystallized and separated from hot hexane as colorless crystals of the guanidine **9** m.p. 119-120°, 320 mg., 80% yield. The hydro-

chloride was made by bubbling hydrogen chloride through a chloroform solution of **9**. After extraction with water, drying and removing chloroform, the colorless hydrochloride was obtained, m.p. 260-261°. Both the guanidine and its hydrochloride were identical with the corresponding products from the photolysis of 3-phenyl-4-cyclohexyloxadiazolone (**5d**). For analysis see Table II.

Photolysis of Oxadiazolones.

Irradiation was carried out in a Rayonet RPR 100 photochemical chamber reactor (Southern New England Ultraviolet Co.) equipped with sixteen low pressure mercury lamps emitting 86% of the total energy of their light in a narrow band at 2537Å and some at 1849Å. During irradiation, temperature in the reactor was 38-43°. Dioxane was purified by refluxing for 3 hours over lithium aluminum hydride and distilling immediately before use.

The solutions of Δ^2 -1,2,4-oxadiazolin-5-ones in dioxane were placed in 550 ml. quartz reaction flasks. Before irradiation was started, the reaction flask and its contents were degassed by passing a stream of nitrogen *via* a sintered glass tube through the solution for at least 6 hours. During irradiation a small stream of nitrogen passed through the solution and carried evolved carbon dioxide into aqueous barium hydroxide. The yield of carbon dioxide was determined by the amount of barium carbonate obtained. All other yields are based on recovered starting material. For each isolated organic product, ir and nmr spectra were identical with corresponding spectra for authentic samples and an undepressed mixture m.p. with authentic material was observed.

Gas chromatographic analyses were carried out on an Aerograph autoprep 700 using either a 5 ft. x 0.25 in. stainless steel column packed with a 20% silicon rubber SE 30 on 60-80 mesh Chromosorb W or a 5 ft. x 0.25 in. glass column packed with 20% carbowax 20 M on an 80-100 mesh Chromosorb W, with helium as carrier gas. A flow rate of 60-70 ml./min. was used. Temperature of the injection port was 200° and of the detector 300°. Yields of small quantities of volatile products were determined by adding benzyl alcohol as an internal standard.

Following irradiation of each oxadiazolone, dioxane was removed from the reaction mixture and an ether or chloroform extract of the residue was analyzed by gc and ir. The product concentrate was treated with either an excess of 6*N* hydrochloric acid or a stream of hydrogen chloride gas followed by aqueous extraction. A chloroform extract of the aqueous acid suspension (or solution) was chromatographically separated from a silica gel column by elution with solvents increasing in polarity from hexane, benzene, chloroform, ether, ethyl acetate to methanol. The aqueous acid solution was made strongly basic by the addition of potassium hydroxide pellets and extracted with chloroform, dried and concentrated. From the concentrate, products were isolated by either recrystallization or by chromatographic separation. Products are found in Table II.

From individual work-ups certain observations require further explanation.

(1) Carbodiimides, if present, were detected by absorption in the 2140-2120 cm^{-1} region by the ir analysis of each crude product mixture. Diphenylcarbodiimide (**2a**) and phenylcyclohexylcarbodiimide, were subsequently isolated as the corresponding ureas (Table II).

(2) An ether extract of the crude product mixture obtained from diphenyloxadiazolone (**5a**) left 2-phenylbenzimidazole as an insoluble solid.

(3) From the aqueous acid solution (suspension) chloroform extracted (as available) cyanamides (resistant to acid hydrolysis), unreacted starting material, carbonyl compounds, nitriles, triazoles,

amides, ureas, triphenyltriazine, and the hydrochloride of the guanidine (**9**). During the chromatographic separation of this chloroform extract from oxadiazolones **5c** and **5d**, a hexane elute containing benzaldehyde and benzonitrile was further separated by a preparative gc column (5 ft., 0.25 in. diameter) of 25% carbowax 20 M on 80-100 mesh Chromosorb W at a column temperature of 140°. Benzaldehyde was led directly into an ethanolic phosphoric acid solution of DNP and isolated as its DNP derivative, m.p. 236-237°.

After hexane-benzene (3:1) had eluted triphenyltriazine (**13**) from the chloroform extract, further chromatographic separation of product from 3-phenyl-4-cyclohexyloxadiazolone (**5d**) gave by elution with hexane-benzene (2:1) 15 mg. of an oil which contained benzonitrile and with hexane-benzene (1:1) a mixture of starting material and cyclohexylphenylcyanamide (**6d**). These were separated by reapplying to a silica gel column and eluting with benzene-hexane (1:2) to remove first the cyanamide, then a mixture, and finally a fraction containing only starting material.

(4) Following elutions with hexane-benzene (3:1), hexane-benzene (2:1), benzene, and benzene-chloroform (6:1) chloroform eluted 3,5-diphenyl-1,2,4-triazole (**10c**) from the chloroform extract obtained from **5c**. The triazole recrystallized from benzene-hexane as colorless needles, m.p. 188-189.5° and showed a molecular ion at m/e (intensity) 221 (100) and a double ion at 110.5 (6), consistent with $\text{C}_{14}\text{H}_{11}\text{N}_3$. Chloroform-ether (1:1) next eluted 3,4,5-triphenyl-1,2,4-triazole (**10c'**) m.p. 292-293° after two sublimations at 200° (1 atm.). Its mass spectrum showed a molecular ion at m/e 297 consistent with $\text{C}_{20}\text{H}_{15}\text{N}_3$. Each of the three **10c**, **10c'** and **10d** were confirmed by independent synthesis.

Following elutions with hexane-benzene (3:1) and hexane-benzene (2:1), hexane-benzene (1:1) removed a mixture of starting material and 3,5-diphenyl-1-cyclohexyl-1,2,4-triazole (**10d**) from the oil obtained from **5d**. Further chromatographic separation of this fraction by benzene-hexane (1:1) afforded the triazole m.p. 106-107° after recrystallization from aqueous ethanol. Consistent with $\text{C}_{20}\text{H}_{21}\text{N}_3$ the mass spectrum showed a molecular ion at 303 (100). Yields are found in Table II.

Anal. Calcd. for $\text{C}_{20}\text{H}_{21}\text{N}_3$: C, 79.17; H, 6.98; N, 13.85. Found: C, 79.30; H, 7.07; N, 13.89.

(5) Following treatment with alkali, *N*, α -diphenylacetamide (**7b**) was extracted by hot hexane from the chloroform concentrate. Partial hydrolysis gave a trace amount of phenylacetamide. The residue, insoluble in hot hexane, gave 2-benzylbenzimidazole on recrystallization from ethanol.

The similar chloroform concentrate from **5c** was chromatographically separated from a column of neutral aluminum oxide, activity I (Beckmann Instruments Inc.) by elution with benzene-chloroform (3:1) to remove 2-phenylquinazoline (**8**). Next, chloroform eluted an unidentified oil, 30 mg., and chloroform-ether (1:1) eluted benzanilide. Finally elution with ether afforded *N*-phenylbenzamide (**7a**) and ethyl acetate followed by methanol removed tar.

On standing, the hydrochloride of *N*-cyclohexylbenzamide (**7d**) (the free base had not been liberated in a solution with pH 11) separated from the chloroform concentrate from **5d**.

Pyrolysis of Oxadiazolones.

3-Benzyl-4-phenyloxadiazolone (**5b**).

After nitrogen was bubbled through 190 ml. of diphenyl ether for at least 5 hours, 1.26 g. (5 mmoles) of the oxadiazolone was added and the solution was heated at reflux, 257°, for 7.5 hours as a stream of nitrogen swept evolved carbon dioxide into aqueous barium hydroxide. As determined by the amount of barium car-

bonate, the evolution of carbon dioxide was quantitative. Removal of diphenyl ether left a dark black-red residue, partially soluble in hexane. After repeatedly treating the chloroform solution with hydrogen chloride gas and extracting with water, chloroform was removed and the residue exhaustively extracted with hot water. The water insoluble portion was dissolved in chloroform and dried.

Chloroform extracts of the water solution treated with an excess of potassium hydroxide pellets were dried and concentrated to give 540 mg. of yellow solid. *N*, α -diphenylacetamidine, 30 mg., 3%, was extracted with hot hexane and recrystallized from benzene-hexane as colorless crystals, m.p. 135-137°. Recrystallization of the hexane insoluble residue from benzene gave 2-benzylbenzimidazole, 460 mg., 44%, as colorless crystals, m.p. 185-187° (22). By chromatographic separation of the remaining acid soluble fractions from an alumina column, a trace of phenylacetamide, m.p. 152-154°, was found.

After removing chloroform from the solution extracted with acid, the dark residue was chromatographically separated from a silica gel column. Several fractions of unidentified oils and a trace of benzylphenylcyanamide (**6b**) were obtained. The cyanamide was identified by a gc retention time identical with that for authentic material and a molecular ion at *m/e* 208.

After heating in diphenyl ether at 257° for seven hours, recovery of the cyanamide (**6b**) in 74% and 2-benzylbenzimidazole in 77%, revealed certain thermal instability of these products. 3-Phenyl-4-benzylloxadiazolone (**5c**).

In a similar manner 2.52 g. (0.01 mole) of the oxadiazolone **5c** was pyrolyzed in 300 ml. of diphenyl ether for 14 hours as the solution became yellow. Carbon dioxide evolution was quantitative. Gc separation of vapors collected at 0.05 mm. in a cooled receiver before diphenyl ether distilled gave benzonitrile, 2.4%, retention time 2.65 minutes (identical for authentic material) and a molecular ion at *m/e* 103, consistent with C₇H₅N.

Removal of diphenyl ether by distillation was followed by treating with 6*N* hydrochloric acid a chloroform solution of the residue. Gc separation of the chloroform solution gave benzaldehyde, 0.9%, identified by its retention time of 2.60 minutes and ir and isolated as its DNP derivative, *vide supra*. Concentration of the chloroform solution brought about the separation of 2,4,6-triphenyl-1,3,5-triazine (**13**) 0.92 g., 44.6%, which recrystallized from hexane as colorless needles, m.p. 231-232°.

Chromatographic separation of the chloroform concentrate, after removal of **13** from silica gel, gave 2,4,5-triphenylimidazole (**14**) 110 mg., 5.2%, m.p. 274-275° after recrystallization from ethanol; a later fraction of 10 mg. brought the yield to 5.7%.

After treatment with an excess of potassium hydroxide pellets, a chloroform extraction of acid soluble fractions was dried, concentrated and separated chromatographically from neutral alumina, activity I. Benzene-chloroform (3:1) eluted 2-phenylquinazoline (**8**) 12 mg., 0.6%, m.p. 97-98.5°, after recrystallization from absolute ethanol. A later fraction was supposed to contain *N*-benzylbenzamidine since a small amount of impure hydrochloride, m.p. 220-224° (lit. (25) m.p. 226-229°) was obtained.

3-Phenyl-4-chlohexyl-oxadiazolone (**5d**).

After 34 hours in 190 ml. of diphenyl ether at 250°, 73% of the theoretical amount of carbon dioxide had evolved from 1.229 g. (5 mmoles) of the oxadiazolone **5d**. Gc separation of vapors collected at 0.13 mm. in a cooled receiver before diphenyl ether distilled gave benzonitrile, 7.1%, and cyclohexanone, 5.4% (a trace of water may have hydrolyzed cyclohexanone imine (s) to the ketone).

A chloroform solution of the residue after removal of diphenyl

ether was repeatedly treated with gaseous hydrogen chloride and extracted with water. From the organic layer, starting material was chromatographically recovered, 24.2%. Chloroform extracts of the aqueous acid fraction after treatment with excess of potassium hydroxide pellets were concentrated. The residue contained *N*-cyclohexylbenzamidine (**7d**) and its hydrochloride salt. A repeated treatment with potassium hydroxide and chloroform extraction afforded the free base **7d**, 61.5 mg., 7.9%, m.p. 114-115°, after reprecipitation from hexane.

Carbodiimides and Cyanamides.

By dehydrosulfurization of an *N,N'*-disubstituted thiourea with yellow mercuric oxide (**40**), diphenylcarbodiimide (**41**), *N*-benzyl-*N'*-phenylcarbodiimide (**42**), *N*-methyl-*N'*-phenylcarbodiimide (**43**), *N*-cyclohexyl-*N'*-phenylcarbodiimide (**44**), and dicyclohexylcarbodiimide (**45**) were prepared (Table III). A sharp absorption in the region 2140-2120 cm⁻¹, characteristic of the -N=C=N- group, was observed for each carbodiimide in chloroform.

With minor modifications of known preparation, diphenylcyanamide (**46**), benzylphenylcyanamide (**47**), methylphenylcyanamide (**47**), and dicyclohexylcyanamide (**48**) were obtained (Table III). A sharp absorption in the region 2220-2200 cm⁻¹, characteristic of the -N-C≡N group, was observed for each cyanamide chloroform.

Cyclohexylphenylcyanamide.

In a two-necked 100 ml. round-bottomed flask, equipped with condenser, calcium chloride drying tube, thermometer, and closed dropping funnel, was placed a solution of 17.5 g. (0.1 mole) of *N*-phenylcyclohexylamine (b.p. 93-95°/0.5 mm.) in 60 ml. of ether. The colorless solution was cooled with stirring in an ice-bath to 0-5°. A solution of 5.3 g. (0.05 mole) of cyanogen bromide in 18 ml. of ether was added dropwise as a colorless precipitate slowly formed. After three hours of stirring at 0-5°, the reaction mixture was stirred an additional 12 hours at room temperature as the solution became pale yellow. A colorless precipitate of *N*-phenylcyclohexylamine hydrogen bromide was collected by filtration on a Büchner funnel with suction, and washed with ether, 12.1 g. (0.047 mole) 47%, m.p. 182-184°.

The yellow ether filtrate was extracted with 2*N* hydrochloric acid to remove unreacted amine. After washing the ether solution with water, it was dried over magnesium sulfate, filtered and evaporated in a rotary evaporator, leaving a brown oil, which distilled at 128.5-129°/0.5 mm. as colorless cyclohexylphenylcyanamide, *n*_D²⁵ 1.5478, 8.3 g. (0.041 mole), 83%, based on recovered starting material. See Table III for other physical properties.

Anal. Calcd. for C₁₃H₁₆N₂: C, 77.96; H, 8.05; N, 13.99; MW 200. Found: C, 77.92; H, 8.11; N, 13.88; M⁺ 200.

Photolysis of Carbodiimides.

Experiments were carried out in a Rayonet RPR 100 photochemical chamber reactor degassed before irradiation by passing a stream of nitrogen *via* a sintered glass tube through the solution for at least 6 hours. During irradiation a small stream of nitrogen was passed through the solution. The reaction mixture in a 550 ml. quartz tube was protected from the air by means of a calcium chloride drying tube. For each isolated organic product, ir and nmr spectra were identical with corresponding spectra for authentic samples and an undepressed mixture m.p. with authentic material was observed.

A solution of 1.04 g. (0.005 mole) of benzylphenylcarbodiimide in 150 ml. of dioxane was irradiated for 36 hours as the solution became a pale brown. Removal of dioxane left a dark brown oil. An ir spectrum (chloroform) showed a very strong

absorption at 2220 cm^{-1} ($\text{C}\equiv\text{N}$) and only a weak absorption at 2140 cm^{-1} ($-\text{N}=\text{C}=\text{N}-$). The brown oil was chromatographed over a column of 60 g. of silica gel. Hexane eluted a small quantity of a pale yellow oil. Its ir spectrum (chloroform) showed a strong absorption at 2140 cm^{-1} ($-\text{N}=\text{C}=\text{N}-$) and resembled that of *N*-benzyl-*N'*-phenylcarbodiimide. Stirring with a few drops of 2*N* hydrochloric acid converted it to a colorless solid, *N*-benzyl-*N'*-phenylurea, 30 mg. (0.13 mmole), m.p. 166-168°, 2.6%. Elution with hexane-benzene (1:2) removed benzylphenylcyanamide isolated as colorless crystals, m.p. 59-60°, 140 mg. (0.67 mmole), yield 13.8%.

Benzene-chloroform (5:1) eluted a small quantity of an unidentified light brown oil, 2220 cm^{-1} ($\text{C}\equiv\text{N}$), whose tlc retention time differed from that for benzylphenylcyanamide. Elution with ether and with methanol gave unidentified brown oils.

Reaction mixtures obtained from the irradiation of other carbodiimides were worked up in a similar way. Results are found in Table III.

By separate experiments it was determined that dicyclohexylcyanamide is photostable under the conditions of photoisomerization of dicyclohexylcarbodiimide. In contrast, diphenylcyanamide is rapidly decomposed by irradiation. Other cyanamides showed intermediate photostability. Carbodiimide absorption in the ir could not be detected after varying amounts of irradiation for any of the cyanamides. A pyrolytic transformation of a cyanamide into a carbodiimide was not detected (49).

Pyrolysis of *N*-benzyl-*N*-phenylcarbodiimide (2c).

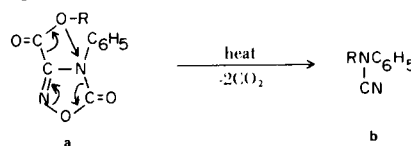
In a 250 ml. two-necked flask, fitted with a condenser, gas inlet and outlet tubes and a heating mantle, was placed a solution of 0.480 g. (2.3 mmoles) of benzylphenylcarbodiimide in 190 ml. of diphenyl ether (m.p. 27-28°). Before heating, the air was displaced by passing a fast stream of nitrogen through the solution for at least 5 hours. During pyrolysis a small stream of nitrogen was passed through the solution. As the solution refluxed for 7 hours (b.p. 260°) it turned deep black. After removal of diphenyl ether (distilled at 80-85° (1.3 mm.)), a deep dark residue was dissolved in 10 ml. of tetrahydrofuran and hydrolyzed with 15 ml. of 3*N* hydrochloric acid. After stirring the emulsion for 30 minutes, it was extracted with chloroform. The combined chloroform extracts were dried over magnesium sulfate, filtered and the dark tarry residue, obtained by concentration of the solvent, was chromatographed over a column containing 60 g. of silica gel. Elution with hexane removed diphenyl ether and hexane-benzene (1:2) gave a yellow brown oil (60 mg.), followed by a red brown oil (30 mg.), whose ir spectrum (chloroform) showed an absorption at 2220 cm^{-1} . After rechromatographing this fraction over 60 g. of silica gel with benzene-hexane (2:1) as eluent, a pale brown oil was obtained which recrystallized from hexane by cooling with dry ice as colorless crystals, m.p. 58-59.5°, 5 mg. (0.024 mmole) of benzylphenylcyanamide, 1.1% yield based on recovered benzylphenylcarbodiimide isolated by transformation into the corresponding *N*-benzyl-*N'*-phenylurea (50). Elution with benzene-chloroform (1:5) produced a small fraction of a brown oil followed by a dark brown oil (220 mg.) from which trituration with ether gave a pale brown solid. It recrystallized from ethanol as colorless crystals of benzylphenylurea (50), 30 mg. (0.13 mmole), 5.6%, m.p. 167-169°. Ether-chloroform (1:5) eluted a colorless solid, m.p. 230-235°, which recrystallized from ethanol as colorless crystals, *N,N'*-diphenylurea (50), m.p. 235-237° (51), 20 mg. (0.094 mmole), 8.6% based on recovered *N*-benzyl-*N'*-phenylcarbodiimide. The urea is presumably formed by hydration of diphenylcarbodiimide, an expected dissociation product from a trimer of benzyl-

phenylcarbodiimide (52). Ether eluted a green oil (30 mg.) and methanol a dark brown oil (70 mg.), both unidentified.

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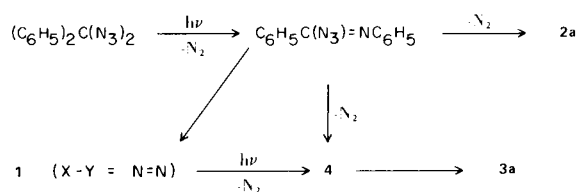
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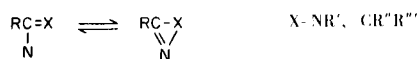
(11) P. A. S. Smith, *Trans. New York Acad. Sci.*, **31**, 504 (1969). To account for the formation of 3a but not 2a (Table I) from 5a and both 2a and 3a from diphenyldiazidomethane by irradiation, it was proposed that 2a results from a rearrangement concerted with elimination of nitrogen from benzimidoyl azide whereas irradiation of diphenyltetrazole gives directly an azomethine nitrene 4 ($\text{R}=\text{R}'=\text{C}_6\text{H}_5$) which gives 3a by cyclization.



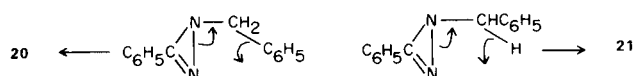
(12) Unpublished results. The possibility that the carbodiimide was generated from a triplet state oxadiazolone or derivative and subsequently gave an adduct with the ketone sensitizer was rejected insofar as the adduct was not detected. A similar photoadduct between an aromatic carbonyl compound and a ketenimine was reported by L. A. Singer and P. D. Bartlett, *Tetrahedron Letters*, 1887 (1964).

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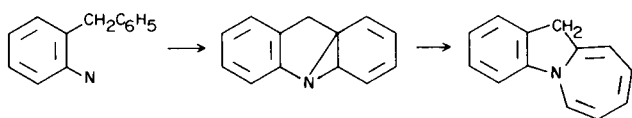
(14a) A possible equilibrium between an azomethine nitrene and a diazirine has been discussed, *ibid.*, pp. 271, 294.



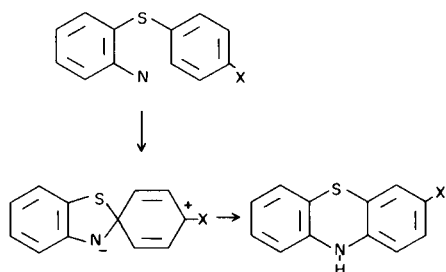
(b) The formation of **20** and **21** may also be explained by a 1,3-migration of phenyl and hydrogen respectively in a diazirine:



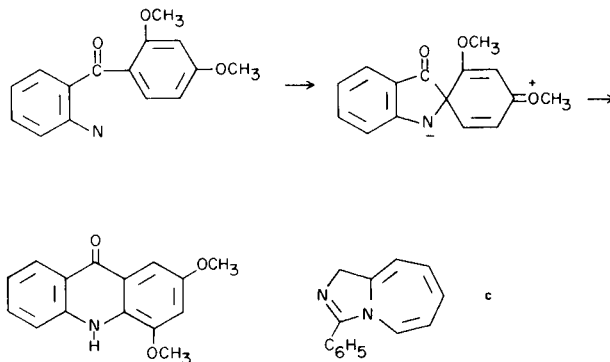
(15) At least three related reactions for aromatic nitrenes have been described: L. Krbeček and H. Takimoto, *J. Org. Chem.*, **33**, 4286 (1968) report:



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Similar reactions from **4c** would produce **c** and/or **8** (after dehydrogenation). There was no evidence for the formation of a seven-membered ring in the present work.

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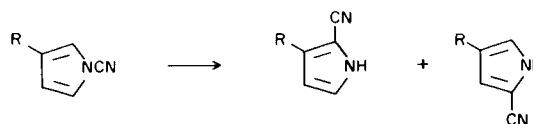
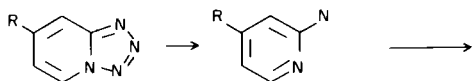
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