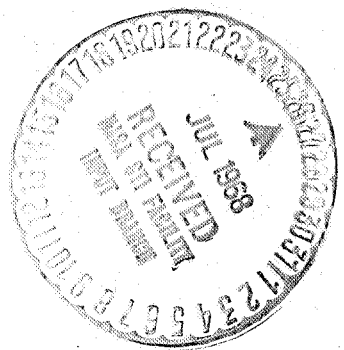


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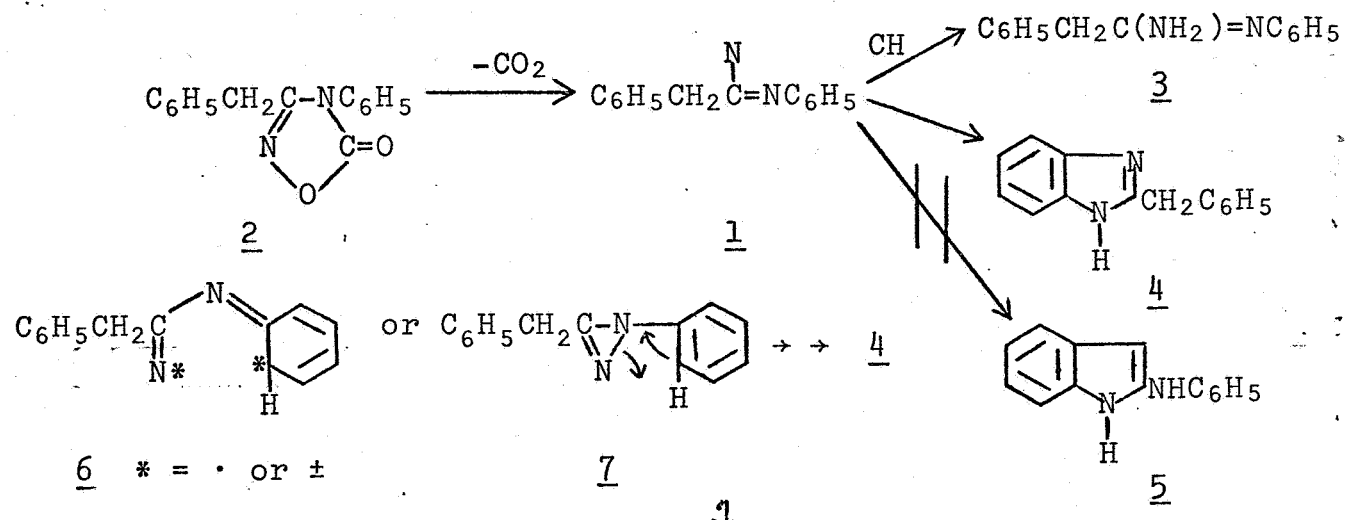
PYROLYSIS AND PHOTOLYSIS OF 3-BENZYL- AND 3-PHENYL-4-PHENYL-1,2,4-OXADIAZOLONE-5

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The intermediacy of an azomethine nitrene, 1, (1) generated from 3-benzyl-phenyl-1,2,4-oxadiazolone-5, 2, by either pyrolysis or photolysis is doubly supported. A subsequent transformation into N,α-diphenylacetamide, 3, through intermolecular hydrogen abstraction is construed as a diagnostic test (2,3), and cyclization through insertion with a CH bond affords the best explanation for the formation of one of two possible five-membered rings. An indiscriminate nitrene could undergo cyclization to form both benzylbenzimidazole, 4, and anilinoindole, 5. Absence of indiscrimination is revealed in the formation of 4 but not 5 and is consistent with ring-closure from either an ionic or biradical form, 6, of the nitrene or from its tautomeric diazirine, 7 (1,4). It is of interest to note that nitrene 1 apparently does not tautomerize into β-anilino-β-styryl nitrene,  $C_6H_5CH=C(NHC_6H_5)N$ .



Heretofore carbodiimides were not detected as either photolytic or pyrolytic products from oxadiazolones (5). In minor amounts, phenylbenzylcarbodiimide, 8, and diphenylcarbodiimide, 9, have been obtained photolytically from 2 and 3,4-diphenyl-1,2,4-oxadiazolone-5, 10, respectively. The corresponding major products are 4 and 2-phenylbenzimidazole, 11. A comparison of product distribution between 2 and 11 generated photolytically and pyrolytically from four different five-membered heterocycles is found in Table I. In addition diphenyldiazidomethane, 15, undergoes photolysis with the formation of 9, 11 and 12 (10). Since photolysis of

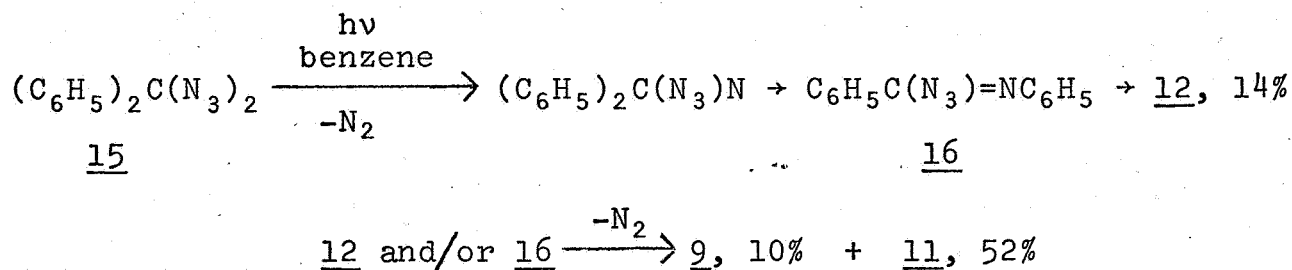
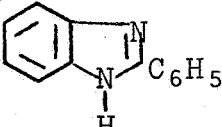
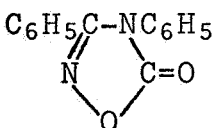
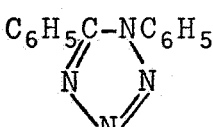
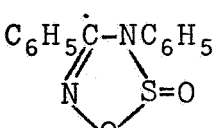
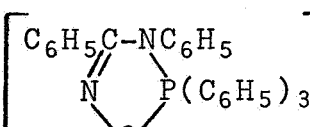


TABLE I

Product Distribution between Diphenylcarbodiimide,  $\text{C}_6\text{H}_5\text{N=C=NC}_6\text{H}_5$ , 9, and

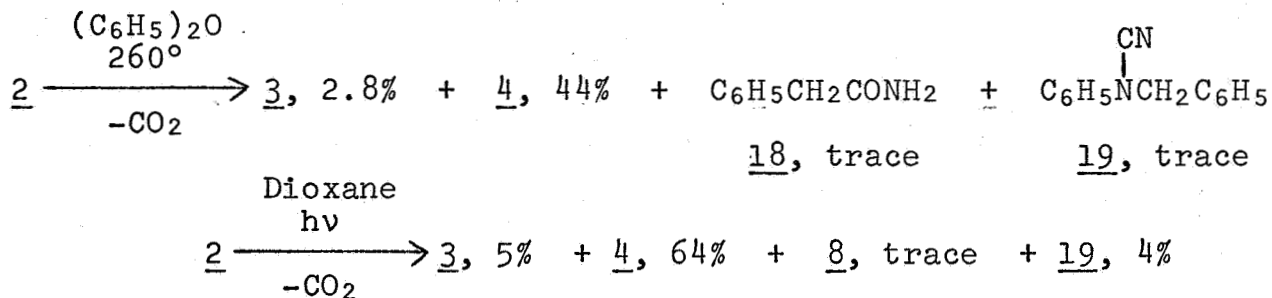
2-Phenylbenzimidazole, , 11.

Starting Material	Number	Product, % Yield		References
		<u>9</u> Pyrolysis Photolysis	<u>11</u> Pyrolysis Photolysis	
	<u>10</u>	0	90	6
		1.1	86	7
	<u>12</u>	76	23	.8
		0	66	3, 9, 10
	<u>13</u>	100	0	11
		62	3	3
	<u>14</u>	100 No data	0 No data	12

diphenyltetrazole, 12, does not lead to the formation of diphenylcarbodiimide, 9, (see Table) it is assumed that the latter arises from the azide, 16, during photolysis of 15.

The product distribution between 9 and 11 from the heterocycles, 10, 12, 13 and 14, and the diazide, 15, is inconsistent with an explanation based on competitive rearrangement from an azomethine nitrene,  $C_6H_5C(=NC_6H_5)N$ , 17, at any given energy level. Competitive rearrangement from the same intermediate at different energy levels, however, is not precluded (13). On the other hand the data is also satisfactorily accounted for if 11 is produced from the nitrene by insertion with an aromatic CH bond (a typical nitrene reaction) and 9 is produced independently of 17, e.g., by a reaction in which rearrangement to the carbodiimide is concerted with an elimination (14). For the tetrazole, 12, simultaneous photolytic cleavage of two ring bonds bringing about the formation of the nitrene, 17, and nitrogen is apparently required. A sequential cleavage would lead initially to the azide, 16, (in an excited state) a precursor for the carbodiimide, 9. Since the latter is not a photolytic product from the tetrazole, 12, a sequential cleavage of tetrazole bonds is unlikely.

An outline of pyrolytic and photolytic products from 2 follows. Photolysis was carried out in a Rayonet unit with light at 2537A. Carbon dioxide was produced quantitatively in each reaction. Apparently phenylacetamide, 18, was produced by hydrolysis of 3 during workup. Phenylbenzylcyanamide, 19, is known to be both a pyrolytic and photolytic product from 8 (15). All starting materials and products were previously known and their identity has been firmly established.



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## References

1. An azomethine nitrene resonance hybrid may be described with the following valence bond structures:
 
$$\begin{array}{c} \text{RC}=\ddot{\text{N}}\text{R} \\ | \\ \text{:N:} \end{array} \longleftrightarrow \begin{array}{c} \text{RC}-\ddot{\text{N}}\text{R} \\ || \\ \text{:N}^* \end{array} \quad (* = \cdot \text{ or } \pm).$$
 A possible valence tautomerism with a diazirine is recognized:
 
$$\begin{array}{c} \text{R}-\text{C}=\text{NR} \\ | \\ \text{N} \end{array} \longleftrightarrow \begin{array}{c} \text{RC} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{NR} \end{array} \quad \text{Spin}$$
 multiplicity for the nitrenes in this work is not established.
2. P.A.S. Smith, Open-chain Nitrogen Compounds, Vol. II, W. A. Benjamin, New York 1966, p. 217.
3. J. Sauer and K. K. Mayer, Tetrahedron Letters 1968, 325. They report the formation of an amidine in 86% yield from the pyrolysis of a mixture of a 1,2,4-oxadiazolone-5 and copper acetylacetonate. Apparently the amidine was not detected from pyrolysis without the catalyst.
4. Extrusion of carbon dioxide from an oxadiazolone may proceed by either simultaneous or sequential cleavage of two ring bonds. Formation of a benzimidazole concerted with ejection of carbon dioxide following cleavage of one ring bond in a 3-substituted-4-aryloxadiazolone is conceivable. Between this extreme and cyclization from a discrete nitrene there may be an infinite number of mechanisms merging into each other, with selection dependent on the requirements of each individual example.  
 The rearrangement required for carbodiimide formation may be concerted with either simultaneous or sequential cleavage of ring bonds. Between these two extremes an infinite number of mechanisms may be merging together. In the event that rearrangement from a nitrene may be required for certain carbodiimide formations there may be an additional family of mechanisms merging between rearrangement concerted with elimination and rearrangement from a discrete nitrene.
5. Benzimidazoles, but neither carbodiimides nor cyanamides, nor amidines, were reported to be pyrolytic and photolytic products from 3-substituted-4-aryl-1,2,4-oxadiazolones by T. Bacchetti and A. Alemagna, Gass. Chim. Ital. 91, 1475 (1961) and in earlier papers.

5. T. Bacchetti and A. Alemagna, Atti acca. nazl. Lincei, Rend, Classe sci. fis., mat. e nat. 22, 637 (1957); Chem. Abstr. 52, 15511 (1958).
7. This is the first report of the photolytic formation of 9 from 10. Previously T. Bacchetti and A. Alemagna (15), and J. Sauer and K. K. Mayer (3) reported the formation of 11 from 10 in 60-75% yields.
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9. W. Kirmse, Angew. Chem. 71, 537 (1959).
10. R. M. Moriarty and J. M. Kliegman, J. Am. Chem. Soc. 89, 5959 (1967).
11. R. Rajagopalan and B. G. Advani, J. Org. Chem. 30, 3369 (1965) proposed the formation of 9 to be concerted with the evolution of sulfur dioxide.
12. R. Huisgen and J. Wulff, Tetrahedron Letters 1967, 921 propose 14 as an intermediate in the reaction between  $C_6H_5CNO$  and  $C_6H_5N=P(C_6H_5)_3$ .
13. J. Sauer and K. K. Mayer (3) assume the competitive rearrangements, 17  $\rightarrow$  9 and 17  $\rightarrow$  11, to account for these products from 10, 12 and 13.
14. Carbodiimide formation concerted with an elimination from 10, 12, 13, 14 and 16 rather than from a rearrangement of the nitrene, 17, is reminiscent of the pyrolytic and photolytic Curtius rearrangement from an acyl azide. S. Linke, G. T. Tissue and W. Lwowski, J. Am. Chem. Soc. 89, 6308 (1967) have concluded that tert-butyl isocyanate formation is concerted with the elimination of nitrogen from pivaloyl azide and does not result from a rearrangement of pivaloyl nitrene, also produced.
15. J. H. Boyer and P.J.A. Frints, Tetrahedron Letters 1968, 3211.