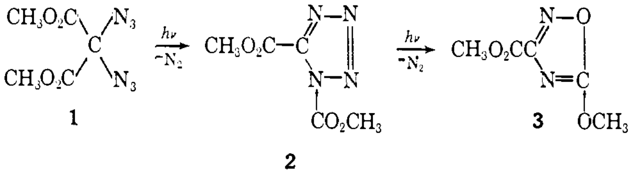
an azidonitrene, a dinitrene, or ultimately a carbene. The first two processes could produce either tetrazoles or diazirines. In view of these manifold possibilities, and also the unusual nature of the starting material[3] and some of the intermediates, we undertook a study of the photolytic reaction.

Irradiation of a 1% benzene solution of dimethyl diazidomalonate (**1**) for 7 hr caused the loss of 1 molar equiv of nitrogen.[4] Disappearance of the azido stretching frequency in the infrared paralleled this change. A small amount of carbon dioxide was also evolved. Continued irradiation led to evolution of a second molar equivalent of nitrogen.

The implication of an initial formation of a product which subsequently loses nitrogen in a second step was confirmed. Interruption of the photolysis after evolution of 1 molar equiv of nitrogen afforded 48% of dimethyl tetrazole-1,5-dicarboxylate (**2**): mp 77–80°; ν_{CCl_4} (cm^{-1}) 1750 (C–CO), 1813 (NCO); δ_{CDCl_3} 4.13, 4.37. The microanalysis and Rast molecular weight determination were correct for $C_5H_6N_4O_4$. The mass spectrum showed no parent molecular ion at *m/e* 186; however, an intense P − 28 peak appeared at *m/e* 158. The behavior is typical of 1,5-disubstituted tetrazoles.[5] Treatment of **2** with 15% sodium hydroxide at 100° for 12 hr yielded tetrazole.[6]

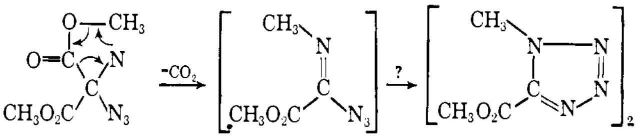


Prolonged irradiation of **1** or separate irradiation of **2** yielded 32% of compound **3**: mp 83–84°; ν_{CCl_4} (cm^{-1}) 1600 (C=N), 1750 (C=O); λ_{max}^{EtOH} 233 mμ (ε 6303); δ_{CDCl_3} 4.00, 4.16. The microanalysis and Rast molecular weight corresponded to $C_5H_6N_2O_4$. The high-resolution mass spectrum showed a parent molecular ion at *m/e* 158.0328; $C_5H_6N_2O_4$ requires 158.0328. The presence of the C–OCH$_3$ group was supported by observation of a peak at *m/e* 128.0248. Loss of CH_2O from $C_5H_6N_2O_4$ requires 128.0222; further a metastable transition at *m/e* 103.7 supports the change 158 → 128 + 30. The isomeric diazirine structure for **3** is unlikely in view of the substantial thermal stability of this compound. Only heating to 150° for 1 hr caused decomposition.

Transformation **1** → **2** requires formal migration of a carbomethoxy group from carbon to nitrogen, a change which is without precedent in photochemistry.

Photochemically induced rearrangement of an N-carboalkoxytetrazole to an oxadiazole, such as **2** → **3**, is unknown; however, a somewhat analogous thermal rearrangement is reported in the formation of 5-acetamido-2-methyl-1,3,4-oxadiazole upon prolonged boiling of 5-aminotetrazole with acetic anhydride.[7,8]

Finally, the observed evolution of small amounts of carbon dioxide in the photolysis prompted us to search for a product which might derive from such a process. A third product was isolated in only 5–7% yield and had mp 110–111°; ν_{CCl_4}(cm^{-1}) 1745; δ_{CDCl_3} 4.04, 4.49 (singlets of equal intensity). The microanalysis and Rast molecular weight agreed with the formula $C_4H_6N_4O_2$ (142). The mass spectrum, however, showed no peak at *m/e* 142, but it did have intense peaks at *m/e* 256 and 225. These data may be accommodated by postulation of loss of both nitrogen and carbon dioxide from **1** to yield an N-methylimino azide which dimerizes, possibly through the tetrazole. The dimer would have the mass spectrum in which one might observe a P − 28 peak as the highest mass fragment if the dimer possesses the azo grouping. The molecular weight determined by the Rast method is an apparent molecular weight due to dissociation of the dimer. Available evidence does not permit formulation of the structure of the dimer, which is still under investigation. It may derive from methyl group migration to yield an N-methylimino azide which may dimerize *via* the tetrazole. Such a rearrangement has some analogy in the photochemical decomposition of α-azidocarboxylic acids and esters.[9]



Acknowledgment. Support of this project under Grant DA-AROD-31-124-G919, Army Office of Research, Durham, N. C., is greatly appreciated. We wish also to thank Dr. A. Mauger, National Institutes of Health, Bethesda, Md., who directed our attention toward diazides. Mass spectral measurements were done by Dr. R. G. Highet, National Institutes of Health, and Morgan and Schaeffer Corp., Montreal, to whom we are greatly indebted.

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(3) Handling of such diazides might appear hazardously adventuresome. Dimethyl diazidomalonate is quite stable to shock, and it can be distilled at reduced pressure. This compound is unexpectedly stable to heat. The synthesis of dimethyl diazidomalonate is interesting and is based upon the method of H. Bretschneider and N. Karpitschka, *Monatsh.*, **84**, 1091 (1953). Reaction of dimethyl monobromomalonate and 1 equiv of sodium azide in methanol yields dimethyl diazidomalonate and dimethyl malonate, but no dimethyl monoazidomalonate. One may envision initial formation of

$$(CH_3O_2C)_2CH\text{—}N_3 \xrightarrow{CH_3OH} (CH_3O_2C)_2\bar{C}\text{—}N_3$$

which could yield the diazido compound by *trans* bromination followed by displacement by azide anion.

(4) A Hanau high-pressure (Q81, 0.5 w at 2800 A) immersion lamp surrounded by a quartz water-cooled heat exchanger was placed directly into the solution. Progress of the reaction was followed either by manometric measurement of the volume of nitrogen evolved or by loss of azide absorption at 2095 and 2120 cm^{-1} in the infrared.

(5) Analogous behavior was observed in the mass spectrum of 1,5-diphenyltetrazole.

(6) O. Dimroth and G. Fester, *Ber.*, **34**, 2219 (1910).

(7) R. Stolle, *ibid.*, **62**, 1119 (1929).

(8) It should be noted that N-carboalkoxytetrazoles are unknown.

(9) R. M. Moriarty and M. Rahman, *J. Am. Chem. Soc.*, **87**, 2519 (1965).

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The Photochemical Decomposition of Geminal Diazides. II. The Solution Photolysis of Benzophenone Diazide

Sir:

In the preceding communication, a reaction sequence was offered for the photochemical decomposition of a geminal diazide.[1] Assuming the identity of the inter-

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(1) R. M. Moriarty, J. M. Kliegman, and C. Shovlin, *J. Am. Chem. Soc.*, **89**, 5958 (1967).

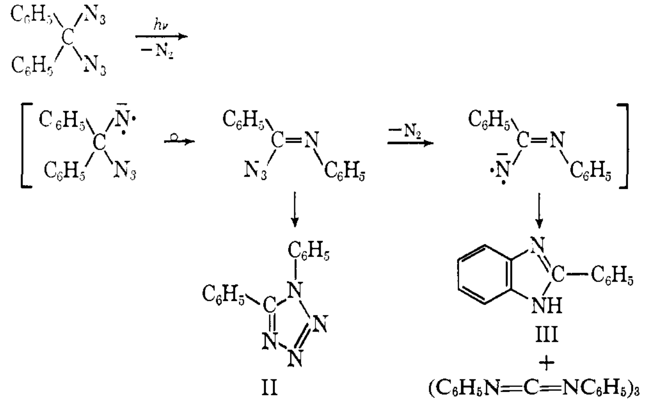
mediates drawn below in brackets, the following steps appeared to occur.

$$\text{diazide} \xrightarrow[-N_2]{h\nu} [\text{azidonitrene} \longrightarrow \text{iminoazide}] \longrightarrow$$

$$\text{1,5-disubstituted tetrazole} \xrightarrow[-N_2]{h\nu} [\text{iminonitrene}] \longrightarrow \text{products}$$

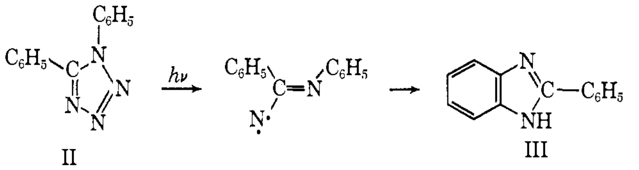
Recently Barash and co-workers reported epr evidence for the intermediacy of the azidonitrene in the photosensitized decomposition of benzophenone diazide (I) in a rigid matrix at 77°K.[2] Furthermore, they report that continued irradiation with light of wavelength 3650 A produced diphenylmethylene which was identified by observation of its epr spectrum. It should be noted, however, that 1,2-carbon-to-nitrogen migration of a phenyl group at the azidonitrene stage would yield an intermediate which *could not be* transformed to diphenylmethylene by any reasonable process. From this viewpoint, the benzophenone diazide system appeared to be a particularly interesting one for the purpose of comparing the course of a photochemical decomposition occurring in a rigid matrix relative to that in dilute fluid solution.

Irradiation[3] of 0.005 mole of benzophenone diazide[4] in 1% benzene solution for 8 hr yielded 2-phenylbenzimidazole (III),[5] 52%, 1,5-diphenyltetrazole (II),[6] 14%, N,N-diphenylcarbodiimide trimer (IV),[5] 10%, along with three unidentified products isolated in minor amounts.



The fact that 1,5-diphenyltetrazole (II) was obtained in the photolysis of I prompted the consideration that III and IV might result from photolysis of preformed II. This was shown not to be the case, however, since irradiation of 0.0033 mole of 1,5-diphenyltetrazole (II) (an amount equivalent to the 1,5-diphenyltetrazole (II) and 2-phenylbenzimidazole (III) produced in the photolysis of I under the same conditions) gave 0.0014 mole of 2-phenylbenzimidazole (III) in 42% yield as the sole product.[7]

It is important to note that no N,N-diphenylcarbodiimide trimer (IV) is formed in the photolysis of II. This result would tend to indicate some difference in the nature of the iminonitrene formed in the photolysis of I compared with the same intermediate which is presumed to be formed in the photolysis of II.



Finally it is clear that a fundamental difference exists between the results obtained in the epr study[2] and those we have found in the fluid solution photolysis of I. The essential difference is that no major products derive from diphenylmethylene in the photolysis of I in dilute benzene solution. Assuming that diphenylmethylene is a major product in the epr study,[2] one must offer an explanation as to why the azidonitrene derived from photolysis of I in a rigid matrix does not undergo phenyl group migration but rather loses two additional molecules of nitrogen to yield the carbene.

It appears most likely that the triplet azidonitrene obtained in the rigid matrix at 77°K very quickly loses any excess vibrational energy which may be required for the phenyl group migration. In benzene solution at room temperature a higher energy azidonitrene occurs which is capable of undergoing chemical reaction, namely, phenyl group migration, before it is deactivated to a ground-state molecule. Furthermore, the required orientation of the phenyl group with respect to the electron-deficient nitrogen may not obtain in the case of an azidonitrene locked in a rigid matrix. Also, the possibility cannot be excluded that the direct photolysis in benzene solution produces a singlet azidonitrene which may react differently from the triplet species. As far as products are concerned, the above results indicate clearly that the subsequent reactions of photochemically generated intermediates, such as azidonitrenes and iminonitrenes, depend strongly upon the mode of formation and environmental factors.

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[2] L. Barash, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **89**, 3932 (1967).

[3] A Hanau high-pressure (Q81, 0.5 w at 2800 A) immersion lamp surrounded by a quartz water-cooled heat exchanger was placed directly into the solution to be irradiated.

[4] Benzophenone diazide was prepared according to the method of S. Götzky, *Ber.*, **64**, 1555 (1931). This compound is dangerous and may detonate upon shock or heat. Never should samples larger than 100 mg be handled.

[5] P. A. S. Smith and E. Leon, *J. Am. Chem. Soc.*, 80, 4647 (1958). These workers carried out the thermal decomposition of benzophenone diazide and obtained diphenyltetrazole. Thermal decomposition of diphenyltetrazole yields the carbodiimide trimer and 2-phenylbenzimidazole.

[6] E. K. Harvill, R. H. Herbst, E. C. Schreiner, and C. W. Roberts, *J. Org. Chem.*, **15**, 662 (1950).

[7] A similar result has already been reported: W. Kirmse, *Angew. Chem.*, 71, 537 (1959).

[8] Author to whom inquiries may be addressed at the Institute of Chemistry, University of Strasbourg, Strasbourg, France.

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Intramolecular Nucleophilic Catalysis of Ester Hydrolysis by the Carboxylate Group

Sir:

We have shown recently that the carboxylate group of aspirin anion is involved in the hydrolysis of the neighboring ester group not as a nucleophile but as a general base.[1] We now report an authentic example of

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[1] A. R. Fersht and A. J. Kirby, *J. Am. Chem. Soc.*, **89**, 4853, 4857 (1967).