which will catalyze the conversion of γ-coniceine to coniine and N-methylconiine are in progress.

[15] On leave of absence from the Instituto De Botanica, Sao Paulo, Brazil.

[16] Work supported by grants from the Medical Research and National Research Councils.

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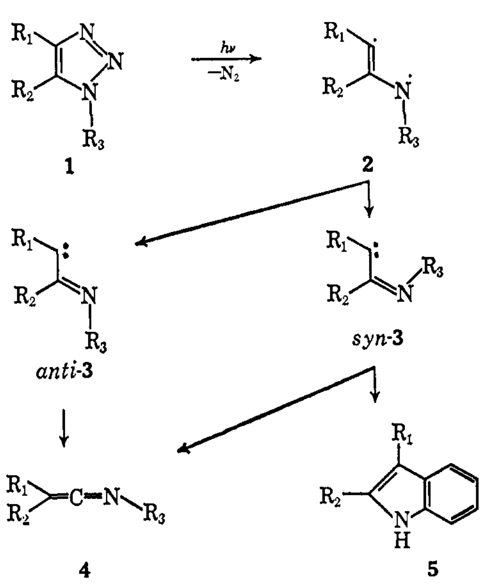
Photochemical Decomposition of 1H-1,2,3-Triazole Derivatives

Sir:

As a possible route to the as yet unknown antiaromatic heterocycle, 1H-azirine, we have investigated the photochemical decomposition of a number of 1H-1,2,3-triazole derivatives. We had hoped that the 1,3-diradical **2** or the carbene intermediate **3** resulting from the photochemical loss[1] of nitrogen from **1** might undergo ring closure[2] to afford this ring system. Although this expectation was not realized, we now wish to report our observations on some interesting subsequent rearrangement pathways available to **2** or **3**.

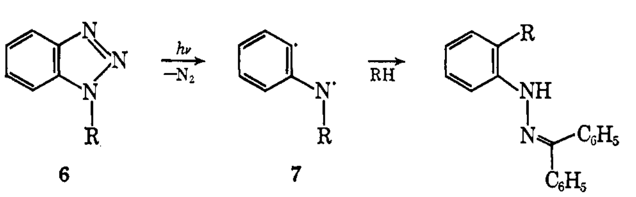


1–5a, $R_1 = R_2 = R_3 = C_6H_5$
b, $R_1 = H$; $R_2 = R_3 = C_6H_5$
c, $R_1 = R_3 = C_6H_5$; $R_2 = H$

The irradiation[3] of **1a**[4] in benzene (10^{-2} *M*) provided a 60% yield of two isomeric products in an equal ratio to which we assigned[5] the triphenylketenimine[6] and 2,3-diphenylindole[7] structures **4a** and **5a**, respectively.

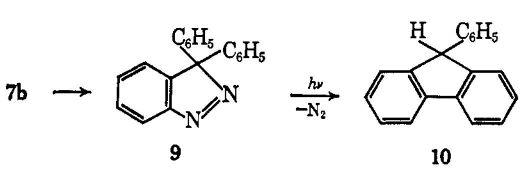
In the same manner photolysis of **1b**[8] afforded a 70% yield of **4b** and **5b**[5,9] in a ratio of 3:1 while **1c**[8] gave 80% of **4b** containing only a trace (<5%) of the indole **5c**.[5,10] The structural assignment of phenylketene-N-phenylimine to **4b** rests upon the observed strong ir absorbance at 2050 cm^{-1}, the appearance of a single vinylic proton at τ 4.84 in the nmr spectrum (60 Mcps, CCl_4), and its hydrolysis to N-phenyl(phenylacetamide).[5] The appearance of the products resulting from 1,2-phenyl or hydrogen migration suggests the intermediacy of the carbenic species **3**. The distribution of **4** to **5** from the photodecomposition of **1a**, **1b**, and **1c** may reflect the partition of **2** between the *syn* and *anti* isomers of **3**, the *syn* stereochemistry being unfavorable in **3a** or **3b** with the *cis*-disposed diphenyl substitution.[11]

In contrast with the above decompositions the photolysis of 1-phenylbenzotriazole (**6a**) in benzene (10^{-1} *M*) gives a nearly quantitative yield of carbazole.[5] The reluctance of the intermediate **7a** to undergo rearrangement[12] or capture by solvent may be attributed to a low barrier to rotation which permits formation of a favorable 1,5-cyclization configuration. Different results are observed in the photolysis of 1-benzhydrylaminobenzotriazole (**6b**). Irradiation of **6b** in benzene (10^{-1} *M*) afforded an 80% yield of benzophenone *o*-biphenylhydrazone[13] (**8a**) while in ethanol only benzophenone phenylhydrazone[5] (**8b**) was isolated. The observed addition of or hydrogen transfer from the solvent implies an radical-like intermediate with a high barrier to internal bond rotation suitable for 1,5 cyclization. An intermediate with a favorable cyclization geometry may be produced in the photodecomposition of **6b** in an inert solvent such as acetonitrile. In this case there was isolated an 80% yield of 9-phenylfluorene (**10**) which presumably arises from ring closure of **7b** to give 3,3-diphenylindazole (**9**) which in a second photochemical step[14] decomposes to give **10**.



6,7a, $R = C_6H_5$
b, $R = (C_6H_5)_2C{=}N$
c, $R = NH_2$

8a, $R = C_6H_5$
b, $R = H$



In this connection it was of interest to examine the photochemical behavior of 1-isopropylidenamino-

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[1] The formation of **2** may be a two-step process *via* the diazoimine, $-N{=}N^+{=}C(R_1)(R_2)C{=}NR_3$.

[2] Such cyclizations have been observed in cyclopropene syntheses: G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Am. Chem. Soc.*, **89**, 3376 (1967); G. L. Closs, W. A. Boll, H. Heyn, and V. Dev, *ibid.*, **90**, 173 (1968).

[3] Photolyses were conducted at ambient temperature using a 450-W Hanovia, high-pressure mercury discharge lamp in a quartz probe.

[4] F. Moulin, *Helv. Chim. Acta*, **35**, 177 (1952).

[5] Identified by infrared spectrum and mixture melting point comparison (where appropriate) with an authentic sample.

[6] C. L. Stevens and G. H. Singhad, *J. Org. Chem.*, **29**, 37 (1964).

[7] C. F. Koelsch, *J. Am. Chem. Soc.*, **66**, 1938 (1944).

[8] W. Kirmse and L. Horner, *Ann.*, **614**, 1 (1958).

[9] R. L. Shriner, *et al.*, *Org. Syn.*, **22**, 98 (1942).

[10] E. Fischer and T. Schmidt, *Ber.*, **21**, 1811 (1888).

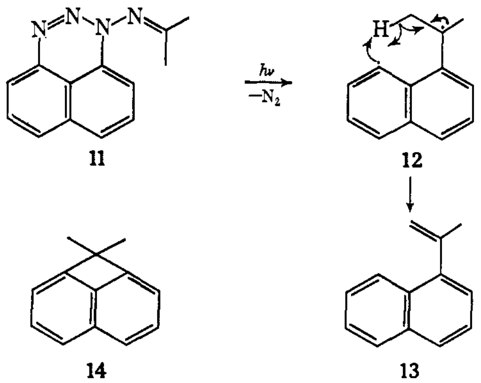
[11] An example of C–H insertion which ocurs exclusively relative to a Wolff rearrangement in a similar carbenic process with favorable stereochemistry may be found in the photodecomposition of 2-diazoacetophenone O-benzyloxime: D. W. Kurtz and H. Shechter, *Chem. Commun.*, 689 (1966).

[12] Ring contraction has been observed in the analogous oxygen system: O. Sus, *Ann.*, **556**, 65, 85 (1944).

[13] Identified by ir and mass spectral analysis.

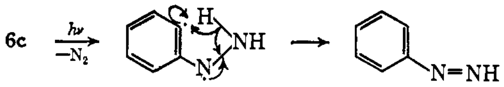
[14] A study of substituted 3H-indazole photodecompositions has recently appeared: R. Bernard and H. Shechter, *J. Am. Chem. Soc.*, **89**, 5307 (1967).

naphtho[1,8-*de*]triazine (**11**).[15] Photolysis of **11** in benzene (2×10^{-2} *M*) provided a 60% yield of 1-isopropenylnaphthalene[5] (**13**) but we were unable to isolate from this reaction the desired 1,1-dimethylcyclobut[1,8-*bc*]naphthalene, **14**.[16] Apparently the 1,4-diradical **12** encounters an insurmountable energy barrier to 1,4 cyclization and a 1,6-hydrogen transfer occurs instead.[17] The perfluoroisopropylidene of **11** upon photolysis in acetonitrile resulted in polymer formation.



11 **12** **14** **13**

In a related decomposition, the irradiation of 1-aminobenzotriazole (**6c**) in benzene (10^{-1} *M*) quantitatively produces biphenyl.[5] A mechanistic proposal for this conversion may involve a 1,5-hydrogen shift in the intermediate diradical **15** to produce phenyldiimide (**16**), whose thermal homolysis is known[18] to produce a phenyl radical which serves as a precursor to the observed product.[19]



15 **16**

Acknowledgment. We wish to thank the National Science Foundation (GP 6719) and the National Institutes of Health (GM 12672) for support of this investigation.

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[15] This compound was conveniently prepared by the Zn–acetic acid reduction of 1H-naphtho[1,8-*de*]triazine in the presence of acetone to afford the acetone 8-aminonaphthylhydrazone, mp 172–173°, which upon treatment with nitrous acid at 0° gave **11**, mp 115°.

[16] The only one-atom 1,8-bridged naphthalene that has been reported is thiet[1,8-*bc*]naphthalene 1,1-dioxide derived from the photolysis of 1,2,3-thiadiazino[1,8-*de*]naphthalene 1,1-dioxide: R. W. Hoffman and W. Sieber, *Angew. Chem. Intern. Ed. Engl.*, 4, 786 (1965); *Ann.*, 703, 96 (1967).

[17] A 1,3 cyclization does occur relative to a 1,4-hydrogen transfer in the photolysis of methyl 3,3-dimethylindazole-6-carboxylate to give dimethyl-3-carbomethoxybenzocyclopropene: R. Anet and F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 525 (1964).

[18] S. G. Cohen and J. Nicholson, *ibid.*, **86**, 3892 (1964); **88**, 2247 (1966); *J. Org. Chem.*, 30, 1162 (1965).

[19] The fate of the hydrogen atom released in the decomposition of **16** is unknown. No reduced reactants were detected in the reaction mixture.

[20] National Science Foundation Undergraduate Research Participant, 1966.

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Periodic Acid–Dimethyl Sulfoxide Mixtures, a Potential Hazard

Sir:

We wish to draw attention to the possibility of an explosion occurring during the preparation of concentrated solutions of periodic acid in dimethyl sulfoxide (DMSO).

In a recent paper[1] the periodic acid–dimethyl sulfoxide system was used to oxidize methyl glycopyranosides and under the conditions reported (0.15 *N* periodic acid in DMSO) there was no evidence of an exothermic reaction.[2] If, however, the periodic acid concentration is increased tenfold, a violent explosion can occur. This was first noticed when periodic acid (34.0 g) was placed in a 100-ml, aluminum-foil-wrapped flask. DMSO was added (*ca.* 70 ml) and the flask was shaken and allowed to stand. After 5–10 min an explosion occurred, shattering the flask.

We were able to repeat this result under the same conditions, in an unwrapped flask, but not when one-tenth of the quantities of reagents was mixed in a small erlenmeyer (25 ml). When the explosion did occur, dense white fumes were evolved, in addition to iodine vapors.

These results suggest great care should be taken when making up periodic acid solutions in DMSO to ensure that heat-dissipation problems do not arise, *i.e.*, by using only dilute solutions and by adding the periodic acid to DMSO in small quantities with adequate mixing and cooling.

This and other reports[3] on the explosive properties of DMSO mixtures suggest room for more work on the exothermic reactions of an otherwise impeccable reagent. The possibility of minor contaminants initiating the explosion should not be overlooked. In this report, reagent grade materials were used, and the DMSO had been purified over calcium hydride.

We are currently investigating the possibility that the heat of hydration of DMSO might, in abstracting the elements of water ($HIO_4 \cdot 2H_2O$) from periodic acid, produce concomitantly sufficiently intense local heat to initiate the explosion.

Acknowledgment. We wish to thank Dr. L. D. Hayward for useful discussions.

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[1] R. J. Yu and C. T. Bishop, *Can. J. Chem.*, 45, 2195 (1967).

[2] Dr. C. T. Bishop, personal communication.

[3] *Chem. Eng. News*, 44, 48 (April 11, 1966).

[4] Teaching Postdoctoral Fellow, 1967–1968, to whom inquiries should be sent.

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Received February 8, 1968

Partial Rate Factors in the Nitration of 10-Methyl-10,9-Borazarophenanthrene[1]

Sir:

In a recent series of papers,[2] we described a novel series of aromatic boron heterocycles, derived from "normal" aromatic compounds by replacing pairs of adjacent carbon atoms by boron and nitrogen, or boron and oxygen. Compounds of this type are of considerable theoretical interest since they are isoelectronic with the "normal" aromatics to which they are related, and a comparison of the properties of such pairs of related structures therefore provides a very

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[1] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

[2] See M. J. S. Dewar and R. Jones, *J. Am. Chem. Soc.*, **89**, 2408 (1967), and references cited there.