Tetrahedron Letters No. 47, pp 4489 - 4492, 1971. Pergamon Press. Printed in Great Britain.

PHOTOLYSIS OF TETRAZOLIDE ANIONS

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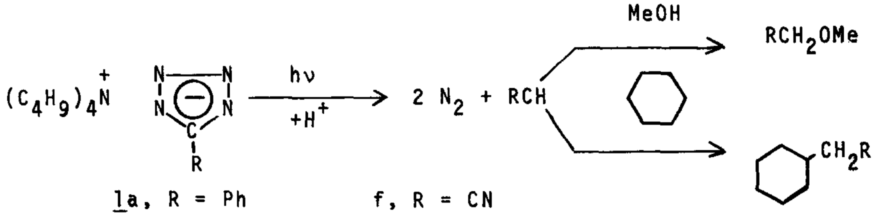
(Received in USA 23 July 1971; received in UK for publication 18 October 1971)

Ultraviolet photolysis of 5-phenyltetrazole produces one equivalent of molecular nitrogen and a dimeric product, dihydro-3,6-diphenyl-_s_-tetrazine.[1] Exclusive dimer formation has been attributed to H-bonding association of the tetrazole substrate.[2] Tetrazolide anions, on the other hand, cannot associate in this manner. In marked contrast to the tetrazole, irradiation of 5-phenyltetrazolide anion (1a) results in two equivalents of nitrogen and products derived from a phenylcarbene intermediate.[1] Further studies have revealed the generality of this reaction and have provided insight into the photodecomposition mechanism.

Deoxygenated solutions (0.03-0.20 M) of several variously 5-substituted tetrabutylammonium tetrazolide salts[3] (1a-i) gave two equivalents of nitrogen on irradiation. With methanol or cyclohexane as solvent, the anticipated



(1)

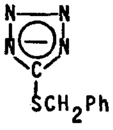
1a, R = Ph
b = H
c = CH_3
d = CF_3
e = _cyclo_-C_3H_5

f, R = CN
g = CO_2Et
h = OEt
i = OPh

O-H or C-H insertion products were obtained in high yield, indicating photolysis _via_ eq (1). Typically, irradiation of 1f in methanol (0.15 M, 100 ml, 254 mμ, 17 hr) gave methoxyacetonitrile, isolated by gc and identified by comparison (IR, retention time) with an authentic sample. Under similar photolysis conditions in cyclohexane, 1f gave cyclohexylacetonitrile.

With the exceptions of the unsubstituted and the 5-methyl tetrazolides (1b, c) the decompositions proceeded efficiently under the conditions employed. However, the presence of dissolved oxygen severely inhibited the rate of nitrogen evolution in all instances. It thus appears that tetrazolide photolysis occurs from the excited triplet state, as was previously demonstrated for 5-phenyltetrazolide anion (1a).[4] The ready availability of 5-substituted tetrazoles and hence their salts suggests synthetic utility for this method of carbene generation.

Although carbene formation was generally observed for the tetrazolide system, photolabile 5-substituents may lead to alternative reaction paths. The major product isolated from 2 was bibenzyl, and 3 underwent photoreduction in protic solvents.[5] The anion of 5-aminotetrazole (4) also photolyzed in an 'anomalous' fashion. Only one equivalent of nitrogen was evolved.

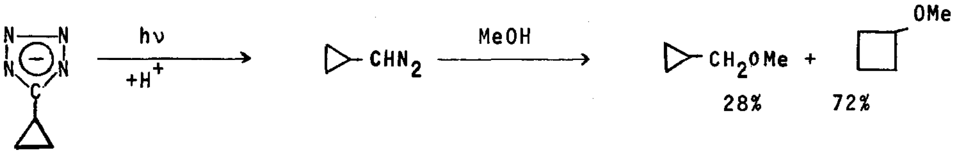


2

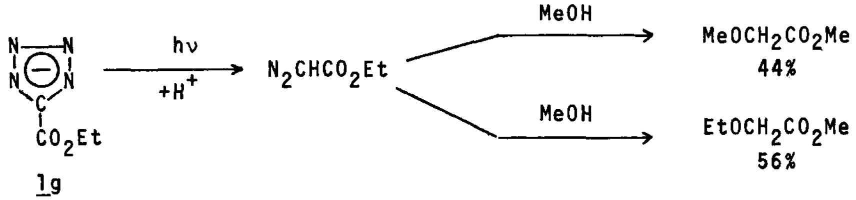
3

4

The appearance of a rearranged product, cyclobutyl methyl ether, from 5-cyclopropyltertrazolide (1e) in methanol suggested the intermediacy of a diazoalkane. Wiberg and others[6] have discussed both the tendency of cyclopropyl-

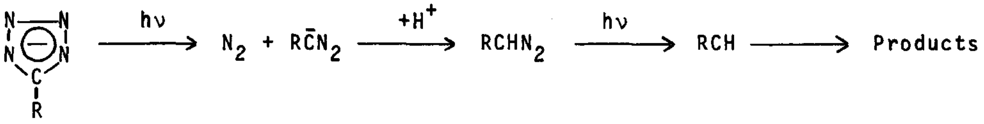


1e



diazomethane to decompose with rearrangement and the facile solvolysis of bicyclo [1.1.0] butane. Further indication of a diazo intermediate was obtained from the photolysis of 5-carbethoxytetrazolide (1g) in methanol. Two methyl esters (based catalyzed transesterification) were formed. The major product, methyl ethoxyacetate, resulting from rearrangement, is characteristic of the photolytic decomposition of ethyl diazoacetate in alcohol solvents.[8]

Interrupted runs (5°, ether-ethanol, 19:1) with 1g provided conclusive spectroscopic evidence for a diazo intermediate. Both IR ($2100 cm^{-1}$) and UV ($248 m\mu$) analysis of the partially photolyzed mixture confirmed the presence of ethyl diazoacetate. Although similar spectroscopic evidence was not obtained with either 1a or 1i, 3-methylpyrazole was detected (gc) among the photolysis products of 5-propenyltetrazolide. The analgous spontaneous rearrangement of diazopropene to pyrazole has been described.[9] It therefore appears probable that tetrazolide photolysis proceeds from the triplet excited state, through the diazoalkane anion to the diazoalkane, and on to products. In the absence of an added proton source e.g.methanol, the diazoalkane anion abstracts a proton from the tetrabutylammonium ion, thus accounting for the previously described formation of tri-n-butylamine.[1]



Acknowledgement. The author gratefully acknowledges the support of the Research Foundation of the City University of New York, Faculty Research Award 1006.

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