HETEROCYCLES, Vol 27, No. 9, 1988

# A UNIQUE FORMATION OF AN ISOXAZOLINE-N-OXIDE FROM NITRODIBROMOACETONITRILE AND TETRAMETHYLETHYLENE

Joseph H. Boyer* and Thanikavelu Manimaran

Department of Chemistry, University of New Orleans, New Orleans, LA 70148

Abstract - Tetramethylethylene and nitrodibromoacetonitrile in dichloromethane at 25°C gave 3-cyano-4,4,5,5-tetramethyl-2-isoxazolin-2-oxide (45%) and 2,3-dibromo-2,3-dimethylbutane (42%).

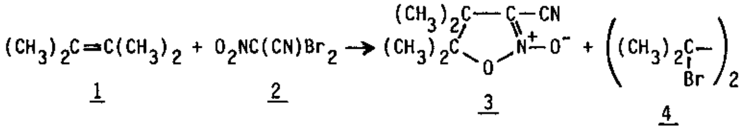
In the first example of the formation of an isoxazoline-N-oxide by a reaction between an olefin and a nitrohalomethane, tetramethylethylene 1 (2 moles) and nitrodibromoacetonitrile[1] (NDBA) 2 in dichloromethane at 25°C gave 3-cyano-4,4,5,5-tetramethyl-2-isoxazolin-2-oxide 3 (45%) and 2,3-dibromo-2,3-dimethylbutane 4 (42%), a known compound,[2] eq(1). The structure of the new heterocycle 3 was confirmed by an X-ray crystallographic analysis.[3]

It is proposed that the reaction proceeded from an intermediate bromonium methide 5/6. Similar abstraction of a "positive" nitro or halo substituent is amply documented for reactions between olefins and tetranitromethane, trinitroacetonitrile, bromotrinitromethane, and iodotrinitromethane.[4,5] The formation of the heterocycle 3 and the dibromide 4 was attributed to a straightforward interaction between the intermediate 5/6 and the olefin 1, eq(2), without differentiation between concerted and stepwise pathways. (Metal salts of negatively substituted derivatives of nitromethane converted olefins in aprotic solvents at 20-50°C to isoxazoline-N-oxides).[4,6]

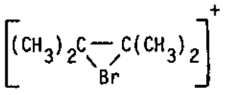
The formations of the heterocycle 3 and the dibromide 4 did not proceed from (a) radical precursor(s) as was shown by a lack of inhibition in product formation by the added presence of either di-*tert*-butylnitroxide or tetracyanoethylene (radical scavengers), an observation supported by an absence of a CIDNP signal for the reaction. Support for the proposed intermediate salt 5/6 was found in the complete suppression of the formation of the heterocycle 3 and no effect on the formation of the dibromide 4 by the added presence of pyridine in the reaction mixture. It was assumed that pyridine converted the intermediate to the dibromide 4 and pyridinium nitrocyanomethylide 7, eq(3), however the latter was not detected in the complex product mixture. Similar treatment converted *trans*-stilbene to *meso*-1,2-dibromo-1,2-diphenylethane, a known compound,[7] but 4,5-diphenylisoxazol-3-cyano-2-isoxazolin-2-oxide was not found.

*The reaction was dependent on the intermediacy of a methide anion with a severely limited ability* to undergo alkylation by the counterion. Neither C- nor O-alkylation was detected. Formation of the heterocycle 3 by ring closure from the β-bromonitronate ester 8 (hypothetical O-alkylation product) was considered unlikely since similar cyclizations from known β-bromonitronate esters 9 did not occur.[5]

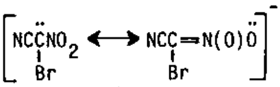
NDBA 2 was chosen for investigation since the cyanonitrobromomethide anion 6 was assumed to be planar and non-nucleophilic as a consequence of the replacement of a nitro group in the cyanodinitromethide anion (planar and nonnucleophilic)[8] with the stereo-comparable bromo group. A consideration of olefins capable of abstracting not only the "positive" bromine from NDBA but also subsequently accepting an ejected bromide anion led to the choice of the electron rich olefin, tetramethylethylene 1.[9]



eq(1)



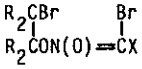
5



6

$$\underline{5}/\underline{6} + \underline{1} \longrightarrow \underline{3} + \underline{4}$$ eq(2)

$$\underline{5}/\underline{6} + C_5H_5N \longrightarrow \underset{\underline{7}}{\left[C_5H_5\overset{+}{N}-\overset{-}{C}(NO_2)CN\right]} + \underline{4}$$ eq(3)



$$\begin{array}{l} R_2CBr \qquad Br \\ R_2CON(O)=CX \end{array}$$

8 R = $CH_3$, X = CN

9 R = alkyl, H; X = $NO_2$

ACKNOWLEDGMENT

Financial support was received from ONR.

REFERENCES

1. W. Steinkopf and L. Boehm, Ber., 1908, 41, 1044.

2. N. S. Isaacs, M. Hodgson, and S. O. Tumi, Tetrahedron Lett., 1981, 22, 4139.

3. We are indebted to Dr. R. Gilardi and Dr. C. George, Naval Research Laboratory, Washington, D.C. for the X-ray analysis. The data will be published elsewhere.

4. J. H. Boyer, "Nitroazoles," Vol. 1 in "Organic Nitro Chemistry," H. Feuer, ser. ed., VCH, Deerfield Beach, Florida, 1986, pp 301-351.

5. K. Torsell, Arkiv För Kemi, 1965, 23, 537 and 543.

6. I. E. Chlenov, M. V. Kashutina, S. L. Ioffe, S. S. Novidov, and A. Tartakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1969, 2085; Eng. p 1948.

7. R. E. Buckles, J. M. Baden, and R. J. Thurmaier, J. Org. Chem., 1962, 27, 4523.

8. (a)L. A. Kaplan and H. B. Pickard, 152nd National Meeting Amer. Chem. Soc., Sept. 1966, paper S9; (b) L. A. Kaplan, "The Synthesis and Reactions of Trinitromethyl Compounds," in "The Chemistry of Nitro and Nitroso Groups," Part 2, H. Feuer, ed. in "The Chemistry of Functional Groups," S. Patai, ser. ed., J. Wiley and Sons (Interscience), New York, 1970, pp 289-328.

9. An extension of this new reaction to other alkenes will be reported later.

Received, 31st March,1988