Tetrahedron Letters, Vol.22, No.17, pp 1639 - 1640, 1981
Printed in Great Britain

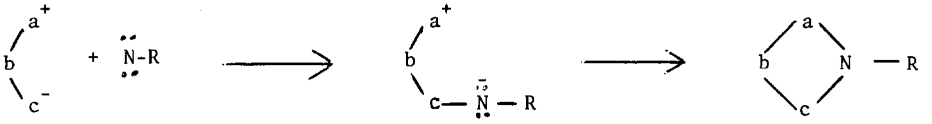
0040-4039/81/171639-02$02.00/0

NITRENE ADDITION TO A MESOIONIC 4-THIAZOLONE. A PROBABLE (1+3) CYCLOADDITION

Tuvia Sheradsky* and David Zbaida
Department of Organic Chemistry, The Hebrew University
Jerusalem, Israel

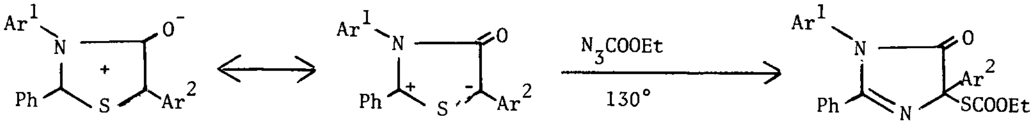
Abstract: The reaction of mesoionic 4-thiazolones with ethyl azidoformate (at 130°) gave 5-(ethoxycarbonylthio)-1-imidazolin-4-ones, probably via a bicyclic nitrene-mesoion adduct.

The use of stable mesoionic compounds as the dipole component in cycloadditions is particularly useful for the study of dipole additions to transient species. We wish to report the first case which probably involves the (1+3) cycloaddition of nitrenes to dipoles. We have expected it to proceed through dipole extension[1], followed by cyclization to a 4-membered ring (equation 1)



(1)

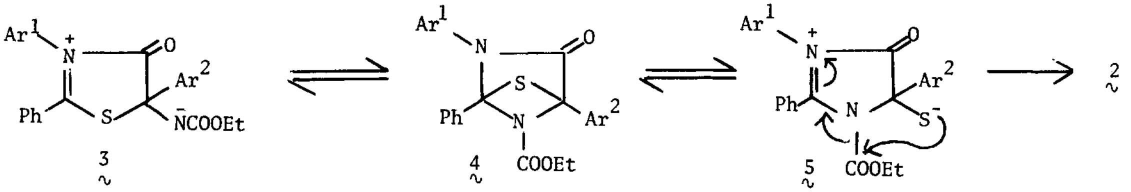
The mesoionic thiazolones(1) were selected as substrates[2], since they have carbon atoms at both ends of the active dipolar form[3]. The reaction of anhydro-4-hydroxy-2,3,5-triphenylthiazolium hydroxide(1a)[4] with ethyl azidoformate (in boiling chlorobenzene, 3.5 hrs) afforded a mesoion-nitrene adduct $(C_{24}H_{20}N_2O_3S)$, m.p. 144° in 45% yield. The product showed I.R. carbonyl absorptions at 1760 and 1705 cm^{-1} and mass spectrum peaks at m/e 311 (rel. intensity 70%, M-105) and 180 (100%). Its structure was established (X-ray, see below) as 5-(ethoxycarbonylthio)-2,3,5,-triphenyl-1-imidazolin-4-one(2a). Similar results were obtained with the chlorinated derivatives[5] 1b (Ar^1=Ph, Ar^2=2-Cl-Ph). 1c(Ar^1=Ph, Ar^2=4-Cl-Ph) and 1d(Ar^1=2,4-diCl-Ph, Ar^2=Ph)[5] which gave 2b(m.p. 122°), 2c(m.p. 151-2°) and 2d(m.p. 148°) respectively[6].



1

2

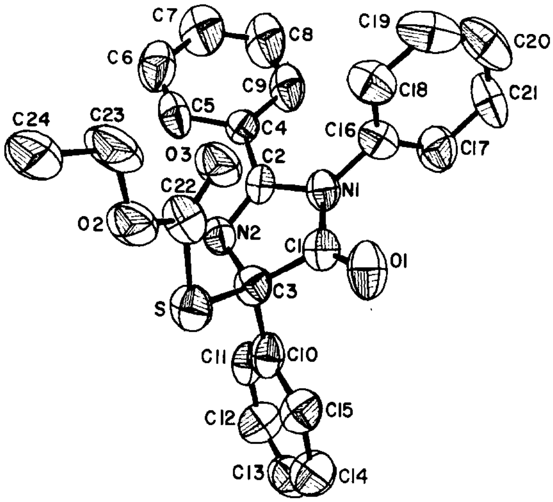
The formation of 2 involves a multi-step process which includes incorporation of nitrogen into the ring, cleavage of a C-S bond and migration of a carbethoxy group from nitrogen to sulphur. The only reasonable reaction path that would accomodate all these transformations included the intermediacy of the highly strained bicyclic system 4. The 4-membered ring in 4 can cleave either reversibly at the C-N bond to the zwitterion 3, or at the C-S bond to the zwitterion 5. Neutralization of the charges can be achieved in 5 by the carbethoxy migration, to form the stable product 2.



The formation of the intermediate 4 represents the first case of (1+3) cycloaddition of dipoles[1]. Further examples and synthetic applications are under study.

Structural assignment: Because of the unusual reaction sequence and unexpected products the structure of 2a was confirmed by single crystal X-ray analysis.

Perspective drawing of 2a (computer generated)



Significant bond lengths (Å)

C_1-O_1	1.1894
C_1-N_1	1.3815
C_1-C_3	1.5318
N_1-C_2	1.4025
C_2-N_2	1.2974
N_2-C_3	1.4518
C_3-S	1.8531
S-C_{22}	1.7542
C_{22}-O_3	1.1935
C_{22}-O_2	1.3364

Crystallography data[7]: Compound 2a gave (from EtOH) monoclinic crystals, space group $P2_1/n$, a=13.393(7) Å, b=10.270(5) Å, c=15.925(4) Å, β=101.60(3)°, z=4. Data were collected on a Philips PW 1100/20 diffractometer (graphite monochromatized Mo Kα radiation). Structure was determined by direct method (MULTAN 78) and refined (SHELX76) on the basis of 1810 reflections $[|Fo|>3\sigma(Fo)]$ to R=0.0807.

References and Footnotes

1) T. Sheradsky and D. Zbaida, J. Org. Chem., 45 4850 (1980).

2) Intramolecular nitrene reactions with several mesoionic systems have been attempted. P.N. Preston and K. Turnbull, J. Chem. Soc. Perkin Transac. II 1229 (1977).

3) K.T. Potts, E. Houghton and U.P. Singh, J. Org. Chem., 39 3627 (1974).

4) K.T. Potts, S.J. Chen, J. Kane and J.L. Marshall, J. Org. Chem., 42 1633 (1977).

5) T. Sheradsky and D. Zbaida, J. Org. Chem., 45 2165 (1980).

6) Correct (± 0.3%) elemental analyses (C,H,N,S,Cl) were obtained for 2a-d.

7) Full data including positional and thermal parameters and their standard deviations, observed and calculated structure factors and bond lengths and angles were submitted for deposition at the Cambridge Crystallographic Data Center. The authors wish to thank Dr. S. Cohen for his help with the X-ray work.

(Received in UK 6 February 1981)