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THE THERMAL FRAGMENTATION OF 1,3,4-DIATHIAZOL-2-ONES

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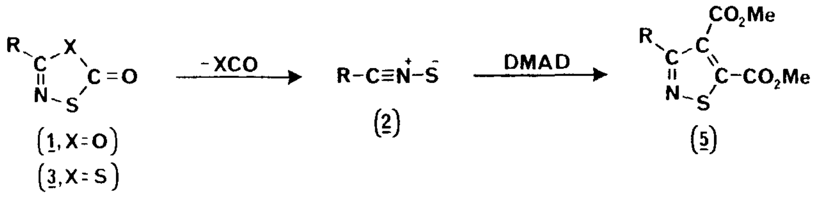
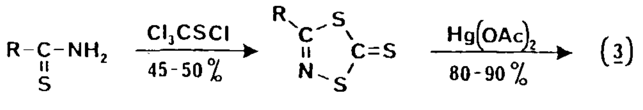
Summary: *Thermal expulsion of carbon oxysulphide from 1,3,4-dithiazol-2-ones in the presence of DMAD affords nitrile sulphide-derived dimethyl isothiazole-4,5-dicarboxylates.*

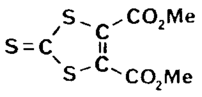
Decarboxylation of 1,3,4-oxathiazol-2-ones (1) has proved[1] to be an effective means of generating nitrile sulphides (2) from which, via their 1,3-dipolar cycloaddition reactions, a variety of C=N-S containing heterocycles may be synthesised. In contrast little attention has been paid to the analogous dithiazolones (3)[2]. We now report that the thermal expulsion of carbon oxysulphide from (3) in the presence of a dipolarophile affords nitrile sulphide cycloadducts.



The 1,3,4-dithiazol-2-ones were prepared by reaction of the corresponding thioamide with perchloromethyl mercaptan (2:1) to yield the dithiazole thiones (4), which were then oxidised by treatment with $Hg(OAc)_2/HOAc/CHCl_3$. The dithiazolone (3,R=Ph) was heated with dimethyl acetylenedicarboxylate (DMAD)(1:10) in mesitylene at 160°C until hplc analysis[3] indicated its complete consumption (after 100 h). Removal of the solvent and excess dipolarophile by distillation under reduced pressure followed by chromatography on silica of the resulting amber oil yielded the isothiazole (5,R=Ph)[4] in 52% yield; identifiable by-products[5] included sulphur, carbon oxysulphide and benzonitrile. Similarly the aliphatic dithiazolone (3;R=Me) afforded (5;R=Me, 56%). In the absence of DMAD the only products detectable were sulphur, SCO and the corresponding nitriles. These results are consistent with fragmentation of (3) to SCO and (2), which either undergo 1,3-dipolar cycloaddition with the dipolarophile or decompose to nitrile and sulphur. The product yields and reaction times are dependent on the electronic nature of the substituent. Treatment at 160^{0}C of a series of 5-aryldithiazolones (5) with DMAD (1:1) gave (5): R=p-MeOC$_6$H$_4$ (60%, 75 h), R=p-MeC$_6$H$_4$ (60%, 90 h), R=C$_6$H$_5$ (55%, 100 h), R=p-FC$_6$H$_4$ (49%, 150 h), R=p-ClC$_6$H$_4$ (46%, 174 h), and R=m-ClC$_6$H$_4$ (48%, 200 h). This behaviour parallels that observed[6] for the oxathiazolones (1), and is indicative of the development of a partial positive charge at the 5-position in the transition state for the expulsion of SCO.



(4)



(6)

In contrast nitrile sulphide derived products are not obtained from (4) under the same conditions, but as previously reported[2], a rapid reaction takes place with DMAD (10 min at 135^{0}C) to yield (6, 76%).

References and Footnotes

1. A.M. Damas, R.O. Gould, M.M. Harding, R.M. Paton, J.F. Ross, and J. Crosby, J. Chem. Soc., Perkin Trans. I, 2991 (1981), and references therein.
2. D. Noel and J. Vialle, Bull. Soc. Chim. France, 1967, 2239.
3. Hplc analysis using silica and CH$_2$Cl$_2$/hexane (70:30); reported reaction times are for the completion of 5-6 half-lives.
4. 70% by hplc analysis[3]. The product was identical to authentic material prepared from (1,R=Ph); mp and mixed mp 72-73^{0}C (J.E. Franz and L.L. Black, Tetrahedron Letters, 1970, 1381).
5. By-products were identified by IR spectroscopy and/or mass spectrometry. SCO, ν_{max} 2060 and 870 cm^{-1}; m/e 60.
6. R.K. Howe, T.A. Gruner, L.G. Garner, L.L. Black, and J.E. Franz, J. Org. Chem., 43, 3736 (1978).

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