Cycloaddition of Dimethyl Acetylenedicarboxylate with 2-Imino-1,3-oxathioles

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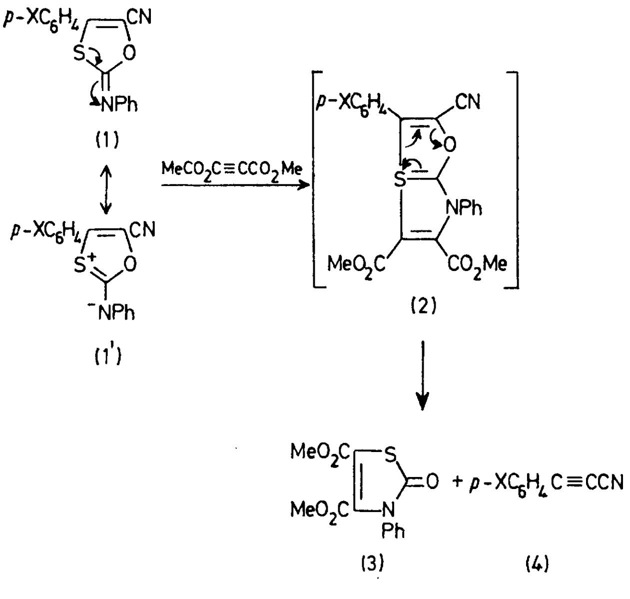
Summary 2-Phenylimino-1,3-oxathioles (**1**), acting as masked 1,3-dipoles with carbon as the central atom, add dimethyl acetylenedicarboxylate to give aryl propionitriles (**4**) and dimethyl 2,3-dihydro-3-phenyl-2-oxothiazole-4,5-dicarboxylate (**3**), probably as a result of thermal decomposition of a 1 : 1 cycloadduct (**2**).

In the course of our study of the addition of thiocarbonyl compounds to *gem*-dicyano epoxides[1] we prepared the imino-oxathioles (**1**).[2] The mesomeric form (**1′**) shows that these compounds are potential 1,3-dipoles with carbon as the central atom. Compounds (**1**) are therefore similar to 3-imino-1,2,4-dithiazoles or 3-imino-1,2,4-thiadiazoles which have been shown recently to add dipolarophiles.[3–5]† We have now shown that the imino-oxathioles (**1**) can also add dimethyl acetylenedicarboxylate (100 h in boiling xylene) to give the thiazolone (**3**), m.p. 125 °C, ν_{max} 1752, 1720, and 1707 cm^{-1}; $\delta(CDCl_3)$ 3·7 (3H, s) and 3·87 (3H, s), *m/e* 293·057 (99% yield), and the aryl propiolonitriles (**4**)[6] [(**4a**) m.p. 41 °C, ν_{max} 2250, 2200, and 2146 cm^{-1}; (**4b**), m.p. 140 °C, ν_{max} similar to (**4b**)] (Scheme). These results may be rationalized by assuming that, in the first step, the reaction leads to the bicyclic tetravalent sulphur compound (**2**) which decomposes in boiling xylene leading to (**3**) and (**4**). In similar reactions described in the literature[3–5] analogous tetravalent sulphur compounds were isolated only in the work reported in ref. 3, where the reaction was carried out at 70 °C for 1–2 h. Methyl maleate or methyl fumarate failed to react with (**1**). We are now attempting to prove whether or not this reaction is truly a 1,3-dipolar cycloaddition.



Scheme
a; X = H
b; X = NO$_2$

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† These reactions are claimed to be 1,3-dipolar cycloadditions but only ref. 5 describes the *cis*-addition of methyl maleate and methyl fumarate with 3-imino-1,2,4-thiadiazoles.

[1] M. Ferrey, A. Robert, and A. Foucaud, *Compt. rend.*, 1973, **277C**, 1153; *Synthesis*, 1976, 261; M. Baudy and A. Robert, *J.C.S. Chem. Comm.*, 1976, 23.

[2] A. Robert and M. Baudy, unpublished results.

[3] K. Akiba, T. Tsuchiya, M. Ochiumi, and N. Inamoto, *Tetrahedron Letters*, 1975, 455.

[4] K. Akiba, M. Ochiumi, T. Tsuchiya, and N. Inamoto, *Tetrahedron Letters*, 1975, 459; J. E. Oliver and A. B. De Milo, *J. Org. Chem.*, 1974, **39**, 2225; J. E. Oliver and R. T. Brown, *ibid.*, p. 2228, and references cited therein.

[5] J. Goerdeler and H. W. Linden, *Tetrahedron Letters*, 1975, 3387.

[6] The phenyl propiolonitrile (**4**; X = H) was not purified, but was identified by g.l.c. comparison with an authentic sample: I. Kazunari and N. Toshio, *Yuki Gosei Kagaku Kyokai sli*, 1970, **28**, 80 (*Chem. Abs.*, 1970, **72**, 900,001q).