Ring Cleavage of 3-Azidothiophens; a Novel Extrusion of Acetylene

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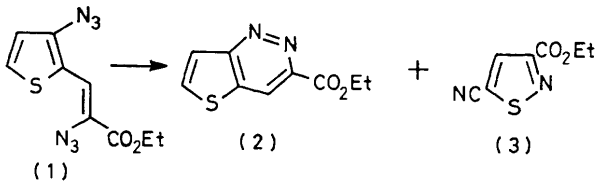
Summary Mild thermal decomposition of the 3-azidothiophen (**1**) results in cleavage of the thiophen ring with extrusion of acetylene and formation of the isothiazole (**3**).

CARBENES and nitrenes derived from aromatic five-membered ring heterocycles are known to undergo ring-opening fragmentation.[1] However, the reported examples of ring cleavage all involve the production of a stable fragment containing nitrogen, either molecular nitrogen or a nitrile; ring fragmentation to give an acetylene has not been observed. We now report a novel extrusion of acetylene from the relatively stable aromatic thiophen ring.

In continuation of our work on vinyl azides,[2] 3-azidothiophen-2-carbaldehyde[3] was condensed with ethyl azidoacetate in ethanolic sodium ethoxide at −15 °C to give

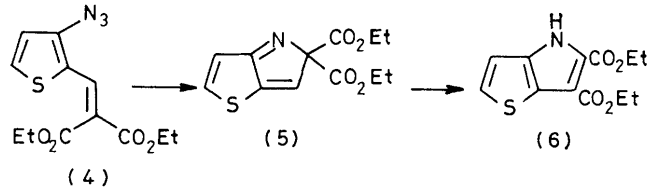


the bis-azide (**1**) (63%).† The azide, m.p. 67—68 °C, decomposed in boiling toluene to give ethyl thieno[3,2-*c*]-pyridazine-3-carboxylate (**2**) (17%), m.p. 129—130 °C, and ethyl 5-cyanoisothiazole-3-carboxylate (**3**) (19%) as an oil after 0·5 h. When the decomposition was carried out in boiling xylene (0·5 h) the yields of (**2**) and (**3**) were increased to 26 and 27% respectively.

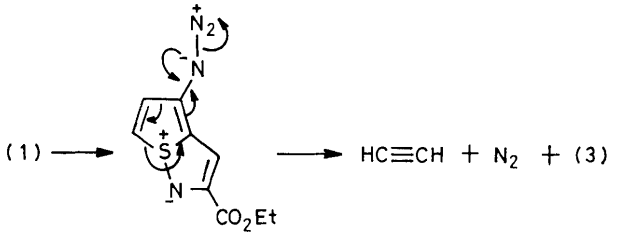
The structure of (**2**) was confirmed by hydrolysis and decarboxylation to give thieno[3,2-*c*]pyridazine, m.p. 95—96°C (lit.,[4] 97·5—98·5 °C). The thieno[3,2-*c*]pyridazine (**2**) is envisaged to arise from coupling of the two azide groups with loss of nitrogen. Despite its apparent simplicity, intramolecular coupling of 'nitrenes' to give N=N is rare. 2,2′-Diazidobiphenyl only gives useful yields of the coupled product, benzo[*c*]cinnoline, when photolysed in a matrix at 77 K.[5]

Hydrolysis and decarboxylation of (**3**) gave the known isothiazole-5-carboxamide, m.p. 169—171 °C (lit.,[6] 172—174 °C). Since the formation of (**3**) requires the loss of nitrogen (2 mol) and acetylene (1 mol), the thermolysis in toluene was repeated and the exit gases bubbled through ammoniacal copper(I) chloride. A red-brown precipitate confirmed the presence of acetylene. The yield of acetylene was 15% (21% in xylene) as estimated by standard methods.[7]

No ring cleavage reactions of 3-azidothiophens have been previously reported, and therefore it seemed likely that the other azide group was playing a key role in the fragmentation of this relatively stable ring. Evidence for the importance of the vinyl azide was obtained from the decomposition of the azidothiophen (**4**). This azide, m.p. 39—41 °C, prepared (96%) by the condensation of the aldehyde with diethyl malonate, gave no acetylene and no ring-cleavage products on heating in toluene. The major thermolysis product was diethyl thieno[3,2-*b*]pyrrole-5,6-dicarboxylate (**6**) (76%), m.p. 110—111 °C, probably formed by a [1,5] shift of the ester group in (**5**).



Therefore, the presence of the vinyl azide is thought to be necessary for ring cleavage under these mild conditions. A possible mechanism would involve initial decomposition of the vinyl azide to give a vinyl nitrene, presumably in equilibrium with the azirine, and co-ordination of the nitrene to the thiophen sulphur, thereby weakening the ring.‡ Loss of acetylene and isothiazole formation may then occur simultaneously (Scheme).



SCHEME

The effect of other vinylic substituents on the decomposition of 3-azido-2-vinylthiophens is being investigated to establish the generality and scope of this ring cleavage reaction.

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† Satisfactory analyses and spectral data were obtained for all new compounds.

‡ The furan analogous to (**1**) decomposed thermally, but gave no acetylene, thus lending support to this proposal.

[1] For example, see T. L. Gilchrist and D. P. J. Pearson, *J. Chem. Soc., Perkin Trans.* 1, 1976, 1257; S.-I. Hayashi, M. Nair, D. J. Houser, and H. Shechter, *Tetrahedron Lett.*, 1979, 2961; G. Kumar, K. Rajagopalan, S. Swaminathan, and K. K. Balasubramanian, *ibid.*, 1979, 4685.

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