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PHOTOCHEMICAL REARRANGEMENT OF A REDUCED DIBENZOTHIOPHEN

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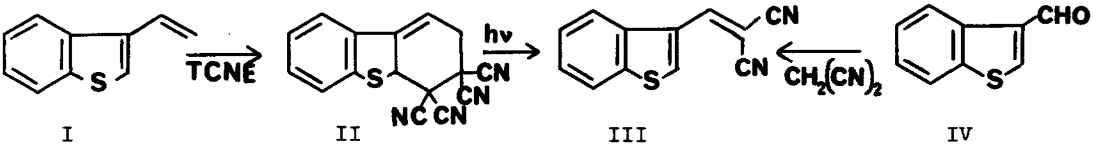
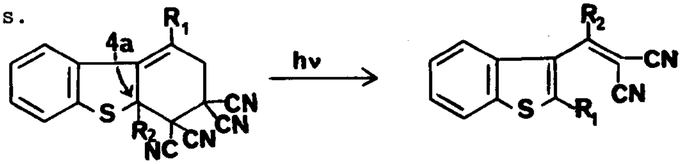
3-Vinylbenzo[b]thiophen (I) has been shown to be a reactive diene,[1-3] and with tetracyanoethylene (TCNE) it gives the adduct (II), whose structure is in accord with its n.m.r. and mass spectra[4]. This adduct is photochemically labile, and when irradiated[5] gave a complex mixture, from which two components have been isolated as pure compounds using thin layer chromatography. The major component (30%) has been allotted structure (III) on the basis of its n.m.r. and mass spectrum[6] and its synthesis from 3-formylbenzo[b]thiophen (IV) and malononitrile[7].



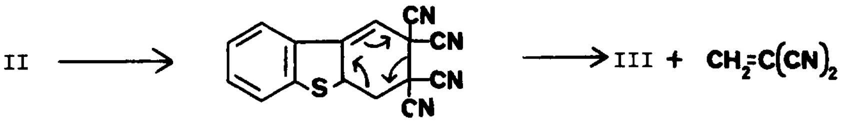
I II III IV

Formation of (III) requires that skeletal rearrangement has accompanied the loss of the elements $CH_2C(CN)_2$, and the isolation of the α-deutero derivative (VI, R_1=H, R_2=D) and 2-methyl-derivative (VI, R_1=H, R_2=CH_3) from irradiations of the mono- deutero (V, R_1=H, R_2=D)[8] and methyl (V, R_1=CH_3, R_2=H)[9] adducts shows that C(4a) in the adduct becomes the α-carbon atom of the β,β-dicyanovinyl group after photolysis.



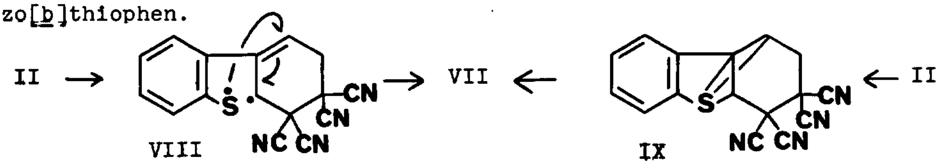
V VI

This rearrangement is most economically explained as resulting from photochemical conversion of the adduct(II)into its isomer (VII), followed by a rapid retro-Diels-Alder decomposition to (III):



VII

So far it has not been possible to isolate (VII). Its formation from (II) may occur via the diradical (VIII) or the expanded valence shell intermediate (IX), and resembles the rearrangements that have been observed to accompany the photochemical addition of dimethyl acetylene dicarboxylate[10] and diphenylacetylene[11] to benzo[b]thiophen.



β,β-Dicyanovinylbenzo[b]thiophen (III) is unreactive as a diene, and it is probable that the adduct (VII) is thermodynamically highly unstable relative to its decomposition products.

The minor product of the photolysis (2%) is isomeric with the starting adduct (II), but is relatively stable thermally and cannot be decomposed to (III).

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4. NMR: δ(CH_3CN, HR-60) 7.70-7.05 (m., 4H), 6.30 (q., 1H), 5.55 (q., 1H) and 3.60 (br.m., 2H). Mass spectrum: (inter alia) $M^{+\cdot}$ (m/e 288), m/e 160, 128 and m*/e 88.7
5. In dry benzene at 30° under nitrogen using a 100 watt medium pressure mercury arc.
6. NMR: δ(DMSO, HA-100) 8.82 (s., 1H), 8.75 (s., 1H), 8.32-8.00 (m., 2H) and 7.65-7.40 (m., 2H). Mass spectrum: (inter alia) $M^{+\cdot}$ (m/e 210), m/e 183 and m/e 159
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8. From TCNE and 2-deutero-3-vinylbenzo[b]thiophen
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