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ANOMALOUS DIELS-ALDER REACTIONS OF 2-METHYL-3-VINYLBENZO[b]THIOPHEN

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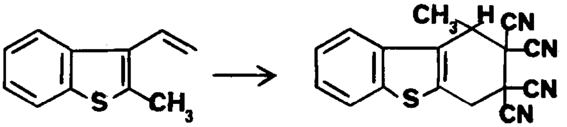
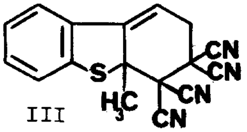
Whereas 3-vinylbenzo[b]thiophen gives normal adducts with a variety of dienophiles,[3,4] including tetracyanoethylene (TCNE),[5] the 2-methyl compound (I) gives an adduct of structure II,[6] rather than III as expected.

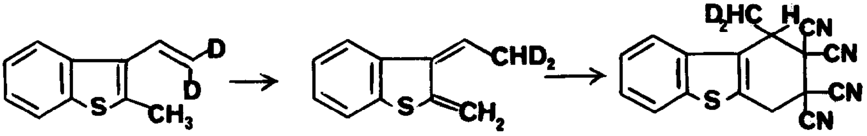


I II



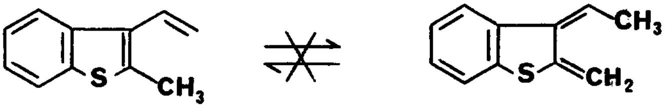
III

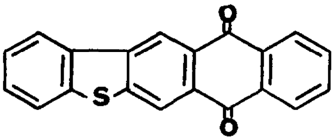
The course of the rearrangement leading to II is clarified by the structure (VI) of the adduct from the dideutero-diene IV[7] and TCNE. The presence of the dideuteromethyl group in VI[8] shows clearly that the methyl group in II is not the original 2-methyl group of I but is formed by hydrogen transfer from (presumably) that methyl group to the methylene group of the 3-vinyl substituent, to give a reactive dimethylene intermediate (V from IV) which then reacts with TCNE.



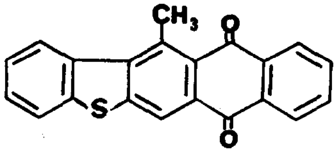
IV V VI

The detailed mechanism of the hydrogen transfer step remains uncertain. When IV is heated in the absence of TCNE no scrambling of deuterium occurs, which counts against the possibility of thermal suprafacial sigmatropic hydrogen shift.[9] Hydrogen scrambling is not catalysed by trace amounts of TCNE or by non-dienophilic charge-transfer reagents such as 1,3,5-trinitrobenzene. Further investigations of this matter are in progress.





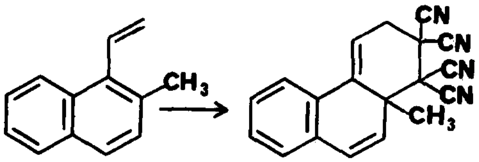
VII



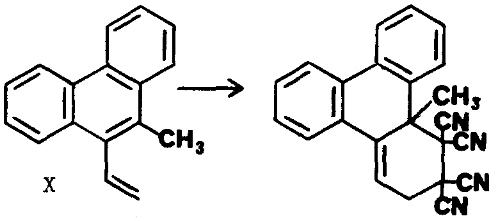
VIII

For steric reasons I is a relatively unreactive diene, and it gives no adduct with maleic anhydride, or with 1,4-naphthoquinone under non-forcing conditions. With an excess of the latter and long heating, a fully aromatic quinone is formed. Its U.V. spectrum[10] is very similar to that of the quinone VII,[4] and it is presumed to be VIII, formed by the same mechanism as is the TCNE adduct, with an added dehydrogenation step.

No rearrangement accompanies the reaction of TCNE and 2-methyl-1-vinylnaphthalene (IX) or 9-methyl-10-vinylphenanthrene (X), and in each case the normal adduct results in fair yield.



IX



X

References

1. Present address: University of Waterloo, Waterloo, Ontario, Canada.
2. On leave from Victoria University of Wellington, New Zealand.
3. W. Davies and Q.N. Porter, J. Chem. Soc., 4961 (1957).
4. T.G. Corbett and Q.N. Porter, Aust. J. Chem., **18**, 1781 (1965).
5. Q.N. Porter and H.G. Upstill, Tetrahedron Letters, 1972, 255.
6. NMR: δ(CD_3CN, HA-100) 1.98 (d, 3H, J=7Hz, CH_3), 4.12 (d, 2H, J=2Hz, $-CH_2-$), 4.34 (q. of t., 1H, J=7 and 2Hz, -CH<), 7.33-7.55 and 7.75-8.00 (m, 4H, aromatic protons). The 2Hz coupling is a CH to CH_2 homoallylic one, c.f. L.M. Jackman and S. Sternhell "Applications of Nuclear Magnetic Resonance in Organic Chemistry" 2nd ed., Pergamon, Oxford, 1969, pp 316 - 328.
7. From 3-formyl-2-methylbenzo[b]thiophen and CD_3MgI then $KHSO_4$.
8. NMR: δ(CD_3CN, HA-100) 2.15 (m, 1H, $-C\underline{H}D_2$), 4.11 (d, 2H, J=2Hz, $-CH_2-$), 4.34 (m, 1H, -CH<), 7.33—7.55 and 7.75-8.00 (m, 4H, aromatic protons). The increase in complexity is the result of D-to-H coupling.
9. R.B. Woodward and R. Hoffmann, J. Amer. Chem. Soc., **87**, 2511 (1965).
10. $\lambda_{max}(CHCl_3)$ 253 (ε 65,000) 271 (57,000) 302 (55,000) and 404 nm (6,900).