

Cyano-substituted 5-Thiabicyclo[2.1.0]pent-2-enes: Reactions and Relevance to Cyanothiophen Phototranspositions

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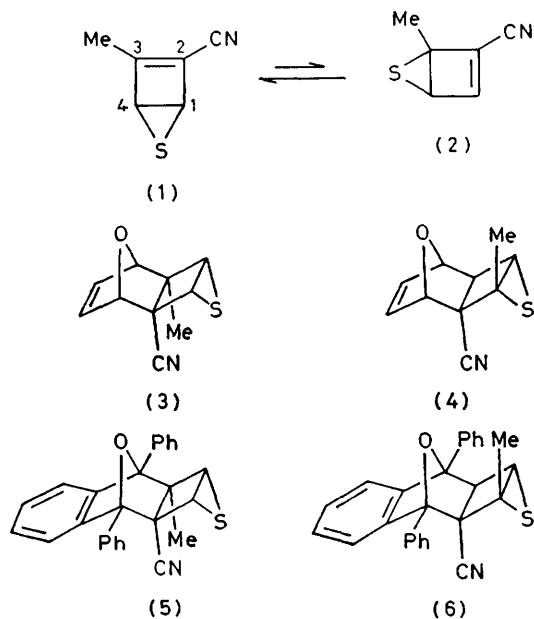
Summary Cyano-substituted 5-thiabicyclo[2.1.0]pent-2-enes have been detected and shown to be intermediates in the phototransposition of cyanothiophens; one such 'Dewar thiophen', 2-cyano-3-methyl-5-thiabicyclo[2.1.0]pent-2-ene, has been isolated and fully characterised, and its aromatisation and rearrangement by sulphur walk, both of which occur photochemically as well as thermally, and its Diels–Alder reactions with furan and 2,5-diphenyl-3,4-benzofuran have been studied.

CYANO THIOPHEN phototranspositions, we have suggested,¹ involve intermediate 5-thiabicyclo[2.1.0]pent-2-enes, which interconvert by walk of the sulphur atom round the carbocyclic ring. Our more recent studies enable us to report here direct evidence for this mechanism and, of more general interest, to describe some of the reactions of a cyanothiophen valence tautomer, 2-cyano-3-methyl-5-thiabicyclo[2.1.0]pent-2-ene (**1**), which is stable enough to be isolated pure at room temperature. The only such 'Dewar thiophen' previously reported is the tetrakis(trifluoromethyl) derivative.²

Irradiation of 0.005 M solutions of either 3-cyano-2-methyl- or 3-cyano-4-methyl-thiophen in cyclohexane with 254 nm light at *ca.* 34 °C in a Rayonet photochemical reactor for 1 h followed by preparative layer chromatography gave, in addition to starting material and transposed thiophens,¹ a yellow oil (6%), λ_{\max} 279 (ϵ 3810) and 340 nm (ϵ 708), which analysed for C₆H₅NS and was assigned the structure (**1**) on the basis of its ¹H n.m.r. spectrum, which had δ (CDCl₃, 35 °C) 2.03 (d, *J* 1 Hz, Me), 3.76 [d, *J* 3.5 Hz, H(4)], and 4.03 [dd, *J* = 1, 3.5 Hz, H(1)].^{†‡} The compound polymerised slowly when kept, but was stable enough in solution to permit n.m.r. studies up to *ca.* 90 °C, above which temperature rearomatisation became appreciable.

The thiabicyclopentene (**1**) reacted at 35 °C with furan in CDCl₃ (5% furan; 8 h) to give quantitatively a 1:1 mixture of the adducts (**3**) and (**4**) together with a small amount (8% of total adducts) of the corresponding *exo*-cyanoisomers.[‡] This result suggests the existence of a dynamic equilibrium between (**1**) and its tautomer (**2**), of which (**3**) and (**4**), respectively, are the expected Diels–Alder adducts.

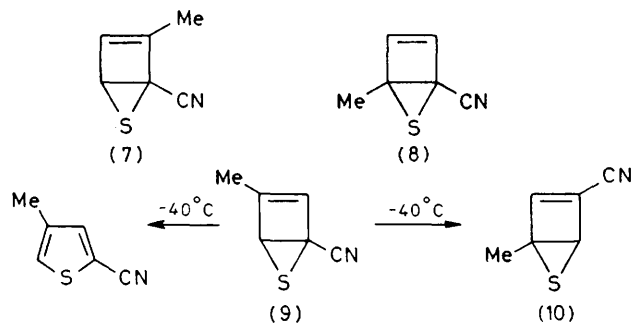
† ‡ For footnotes, see p. 967.



However, the absence of n.m.r. evidence for (2) over the temperature range -80 to $+90$ °C implies that (2) constitutes only a very small fraction of the equilibrium mixture, probably because this isomer lacks the stabilising effect of a methyl group on the double bond. The rate of interconversion of (1) and (2) at 35 °C must, however, be at least comparable with that of furan addition to (1) to allow formation of (4) from (2); in that situation, the much greater dienophilic reactivity expected⁵ of (2) readily accounts for the formation of equal amounts of the adducts (3) and (4). In support of this interpretation, the highly reactive and much less selective reagent, 2,5-diphenyl-3,4-benzofuran, reacted virtually instantaneously with (1) in CDCl_3 at 35 °C to give exclusively and quantitatively the adduct (5) derived from the predominant tautomer (1).

Direct evidence for the existence of (2) and its thermal isomerisation to (1) was obtained by 254 nm irradiation of 3-cyano-2-methylthiophen in $[\text{2H}_8]$ tetrahydrofuran (THF) at -68 °C. After 3 h, n.m.r. spectroscopy at -70 °C indicated 35% conversion into a 1:3 mixture of (1) and (2).[§] Upon warming, (2) isomerised rapidly to (1) ($t_{1/2}$ 2 min at -35 °C). A similar 3-cyano-2-methylthiophen solution, when treated, following irradiation at -68 °C, with 2,5-diphenyl-3,4-benzofuran at -68 °C for 5 min, then allowed

to warm up to room temperature, gave in 1:1.2 ratio the adducts (5) and (6) derived from (1) and (2), respectively. Further evidence for the initial generation of (1) and (2) in non-equilibrium proportions was obtained by irradiation of 3-cyano-2-methylthiophen in furan at -40 °C, which gave the adducts (3) and (4) in the ratio 1:10.[¶] In contrast, a similar experiment at $+34$ °C gave (3), (4), and the corresponding *exo*-cyano-adducts in exactly the same proportions as noted above for the thermal reaction of (1) with furan at $+35$ °C.



Weak additional n.m.r. signals observed at δ 2.11 (d, J 1.5 Hz, Me), 4.68 (br s, 1H), and 6.29 (m, 1H) following irradiation at -68 °C of 3-cyano-2-methylthiophen in $[\text{2H}_8]$ THF were tentatively assigned to the 1-cyanothiabicyclo[2.1.0]pent-2-ene (7). This species disappeared very rapidly at -35 °C. Its probable fate can be inferred from the fact that, when the thiabicyclo[2.1.0]pent-2-ene (9) and (10) were generated in an analogous low-temperature irradiation of 3-cyano-5-methylthiophen, the 1-cyano-isomer (9) was observed to decay rapidly at -40 °C to the 2-cyano-isomer (10) and 2-cyano-4-methylthiophen.^{††}

It is unlikely that (7) (or 8) exists to any real extent in thermal equilibrium with (1) and (2) at room temperature, since prolonged treatment (2 days) of (1) with the inverse-electron-demand diene, hexachlorocyclopentadiene,^{5,6} yielded no adduct. However, this cannot be the case at higher temperatures, since pyrolysis of (1) at 170 °C gave all four methylcyanothiophenes that are, in principle, accessible from (1) by sulphur walk *via* (2), (7), and (8) and/or rearomatization, in the proportions shown in the Table. [The comparable results shown in the Table for the pyrolysis of the 1:1 mixture of (3) and (4) lend support to our previous suggestion¹ that the pyrolysis of such furan adducts regenerates the corresponding thiabicyclo[2.1.0]pent-2-enes.]

[†] 2-Cyano-5-thiabicyclo[2.1.0]pent-2-ene itself, δ (CDCl_3 , 35 °C) 3.83 [d, H(4)], 4.15 [dd, H(1)], and 7.14 [d, H(3)] ($J_{1,4} = J_{1,3} = 4$ Hz), was detected in small amount upon irradiation (254 nm, $+34$ °C) of 3-cyanothiophen in cyclohexane. It gave the expected¹ adducts upon treatment with furan, but was too unstable to be isolated.

[‡] The *endo*-CN adduct mixture (m.p. 76 – 78 °C) analysed correctly for $\text{C}_{10}\text{H}_9\text{NOS}$ and had the expected n.m.r. spectrum, but could not be separated. However, the corresponding tricyclic dienes obtained by desulphurisation with trimethyl phosphite were separable by g.l.c. Their n.m.r. spectra resembled that of the previously described analogue.⁴ In both *exo*-CN adducts, the furan residue was situated *anti* to the thi-iran ring (*cf.* the stereochemistry of the related *exo*-CN adduct obtained by irradiation of 3-cyanothiophen in furan¹). The *exo*-CN analogues of (3) and (4) were formed in the ratio 3:1, respectively, presumably for steric reasons.

[§] (2) had δ 2.04 (s, Me), 4.26 [s, H(4)], and 7.48 [s, H(3)]. In $[\text{2H}_8]$ THF at -70 °C, (1) had δ 2.01 (Me), 4.42 [H(1)], and 4.12 [H(4)], with the same coupling constants as observed in the CDCl_3 spectrum at $+35$ °C.

[¶] In this experiment, no attempt was made to detect the corresponding *exo*-CN adducts.

^{††} Only very tentative evidence for thiabicyclo[2.1.0]pent-2-enes was obtained upon irradiation of 2-cyanothiophenes. Thus, irradiation of 2-cyanothiophen in a THF- CH_2Cl_2 glass through quartz at 75 K with a high-pressure mercury-arc lamp resulted in a 30% decrease in the intensity of the CN stretching band at 2225 cm^{-1} and the appearance of a shoulder at 2235 cm^{-1} , which might be attributed to the CN group in 1-cyanobicyclo[2.1.0]pent-2-ene. Upon warming, the shoulder disappeared between 130 and 138 K, whereupon the 2225 cm^{-1} band regained most of its original intensity. Lacking conjugative stabilisation, 1-cyanothiabicyclo[2.1.0]pent-2-enes are apparently much less stable than the 2-cyano-isomers.

Irradiation of (1) at 254 nm in ether at 34 °C rapidly gave the four accessible cyanothiophens (see Table). Since the cyanothiophens interconvert upon irradiation at 254 nm,¹ but have negligible absorptions above 290 nm, the second experiment recorded in the Table, irradiation through Pyrex with a medium-pressure mercury-arc lamp, probably reflects more truly the intrinsic photochemical behaviour of (1).

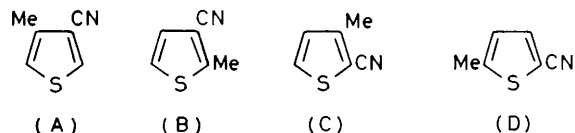


TABLE. Rearomatisation of (1) under various conditions.

Reactant	Conditions	Product ratios			
		(A)	(B)	(C)	(D)
(1)	$h\nu$ (254 nm)	100	10	32	35
(1)	$h\nu$ (>290 nm)	100	10	12	0.2
(1)	Heat (170 °C)	100	52	15	5
(3) + (4)	Heat (170 °C)	100	57	12	10

Thus, both sulphur walk and rearomatisation of cyanothiabiacyclo[2.1.0]pent-2-enes can be induced photochemically. In this respect these species resemble their all-carbon analogue, bicyclopentene,⁷ but whether walking occurs photochemically by simple [1,3] sigmatropic shift

(as may be the case for bicyclopentene,⁷ but see ref. 8), or by some other process, is unknown. The case of bicyclopentene⁹ also provides analogy for the thermal rearomatisation of cyanothiabiacyclopentenes, but apparently not for their facile thermal interconversion by sulphur walk. The closest analogy for the latter reaction is the degenerate rearrangement of tetrakis(trifluoromethyl)-5-thiabiacyclo[2.1.0]pent-2-ene, which has been studied between 94 and 189 °C by ¹⁹F n.m.r. spectroscopy^{2d} and described as a 'pseudopericyclic' process.^{2d,e} This perfluorinated analogue, however, is remarkably resistant to thermal rearomatisation ($t_{1/2}$ 5.1 h at 160 °C),^{2b} and it is also stable to irradiation (at 214 nm).^{2a}

In the phototranspositions of cyanothiophens, then, it seems that, following the initial photochemical act of 2,5-bonding, both photochemical and thermal processes are implicated, the latter revealing themselves mainly by a pronounced temperature effect upon the efficiency of transposition.

The behaviour of the sulphoxide derived from (1) by treatment with *m*-chloroperoxybenzoic acid (*cf.* the tetrakis(trifluoromethyl) analogue^{2d,e}), and attempts to convert (1) into metal complexes of 1-cyano-2-methylcyclobutadiene will be reported later.

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