Phototranspositions of Cyanothiophens: Permutation Pattern Analysis and the Chemical Trapping of an Intermediate 5-Thiabicyclo-[2.1.0]pent-2-ene

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Summary Through their first excited singlet states, cyanothiophens undergo phototranspositions for which permutation pattern analysis and the isolation of furan–thiabicyclopentene adducts from irradiations in furan suggest a mechanism involving 2,5-bonding followed by a 'walk' of the sulphur atom.

Previously observed phototranspositions of thiophens present a complex mechanistic picture.[1] We report here that cyanothiophens and their methyl homologues show relatively simple photochemical behaviour, undergoing transposition by a sulphur 'walk' mechanism.

Thus, irradiation of 0.01 mol l^{-1} solutions of 2-cyanothiophen with 254 nm light at *ca.* 34 °C in a Rayonet photochemical reactor resulted in slow conversion into 3-cyanothiophen; similarly, irradiation of 3-cyanothiophen gave the 2-isomer.† Transposition probably involves the lowest excited singlet state ($\pi\pi^*$ from solvent shifts of the u.v. absorption spectra), since neither conversion could be effected by population of the triplet state.‡

† In ether, cyclohexane, methanol, and acetonitrile, the relative initial rates for both isomers were 1:0·5:0·5:1·3, respectively. In ether, 5% destruction of the starting material occurred in 6 h, giving 1% and 2·5%, respectively, of phototransposition of the 2- and the 3-isomer. In all solvents, continued irradiation led to extensive polymerisation. In no solvent was thiophen itself detected; intermolecular pathways for the transposition seem therefore to be excluded.

‡ 2-Cyanothiophen quenched the photoreduction of benzophenone by benzhydrol; 3-cyanothiophen failed to quench this reaction, but did quench the photoreduction of acetophenone. Thus, 2-cyanothiophen has $E_T < 69$, and 3-cyanothiophen has $69 < E_T < 74$ kcal mol^{-1} (1 cal = 4·184 J). In none of these experiments was any transposition observed. Penta-1,3-diene quenched the phototranspositions only slightly (2-cyano: 15% quenching by 0·4 mol l^{-1} diene; 3-cyano: 19% quenching by 1·2 mol l^{-1} diene), presumably by direct deactivation of S_1.

TABLE. Permutation patterns in methyl-2-cyano- and -3-cyano-thiophen transpositions.

Reactant	Products and their formulation patterns[a]					
	(8)	**(9)**	**(10)**	**(11)**	**(12)**	**(13)**
(8)	b	A, B[c]	C, D	E, F	—	—
(9)	A, G[c]	b	F, H	C, I	—	—
(10)	A, G[c]	H, F	b	C, I[d]	—	—
(11)	E, F[c]	A, D[d]	B, C[d]	b	—	—
(12)	—	—	—	—	b	C, F
(13)	—	—	—	—	A, F	b

[a] Entries indicate the possible ring permutations giving rise to each product from the specified reactant. The permutation patterns are illustrated in formulae A—I, in all of which the 2- or 3-cyano-group of the reactant is taken as being on the right hand side of the ring. [b] Starting material. [c] Major product. [d] Trace product.

The complete set of monomethyl homologues was irradiated similarly to low conversion with the permutation pattern[2,3] results shown in the Table.§ The methylated 2-cyano isomers underwent markedly slower transposition than 2-cyanothiophen itself, but the rates were enhanced appreciably by irradiation at a higher temperature (80 °C) in acetonitrile.
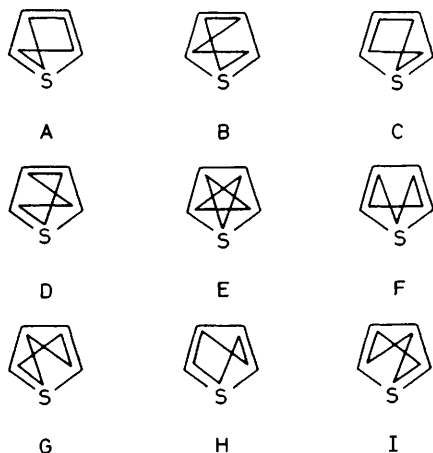
The conversion of 3-cyano-4-methylthiophen into the 3-cyano-2-methyl isomer occurs by permutations **A** and/or **B**, and of 3-cyano-2-methylthiophen into the 3-cyano-4-methyl isomer by permutations **A** and/or **G**. Hence, with the assumption that the methyl groups function merely as positional labels, the simplest inference is that 3 → 3-cyano conversion occurs by permutation **A**, which is common to both cases. Analogously, the 2 → 2-cyano conversions have permutation **C** in common. In contrast, there is no common permutation for either the 2 → 3-cyano or the 3 → 2-cyano conversions. For the 2 → 3-cyano conversion, therefore, we have to ask what is the simplest hypothesis consistent with the observations that: (i) the 2-cyano-3-methyl isomer permutes by **A** and/or **G** and **H** and/or **F**; (ii) the 2-cyano-5-methyl isomer by **E** and/or **F** and **A** and/or **D**; and (iii) the 2-cyano-4-methyl isomer by **A** and/or **F**. In Boolean terms[4] (with plus = inclusive 'or' and multiplication = 'and'), these observations are representable by (**A** + **G**) (**F** + **H**) (**E** + **F**) (**A** + **D**)

(**A** + **F**), which reduces, with the aid of the law of absorption [$p(p+q) = p$; i.e., if $x \supset a$, then $ax = a$], to **A.F** + **A.E.H** + **D.F.G**. The first product, **A.F**, has the fewest terms, and hence the minimum postulate accounting for all the 2 → 3-cyano conversions is the pair of permutations **A** and **F**. Similarly, for the 3 → 2-cyano conversions, the minimum postulate is **C** and **F**. To account for all the observed phototranspositions in the Table, we need as a minimum the three permutations **A**, **C**, **F**.
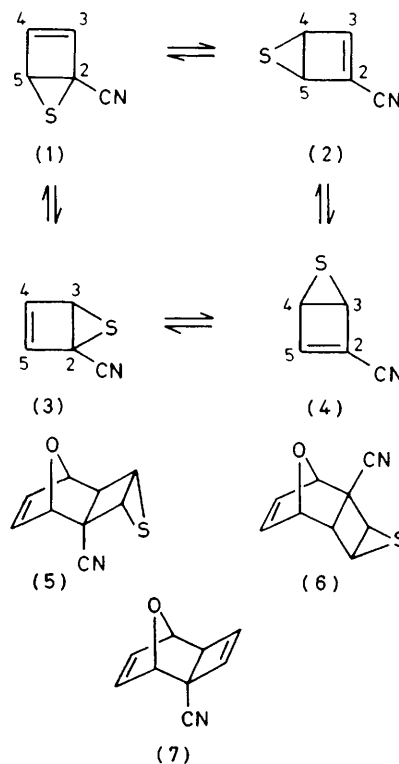
The common feature of **A**, **C**, and **F** is that all three preserve the sequential order of the ring carbon atoms, the only difference being where the sulphur atom is inserted within that sequence. This is consistent with a mechanism in which 2,5-bonding in the first excited state of the reactant gives rise to a set of intermediate 5-thiabicyclo-[2.1.0]pent-2-enes (1—4) interconverting by a 'walking' of the sulphur atom round the carbocyclic ring at a rate comparable with that of rearomatisation.

In support of this mechanism, irradiation of 3-cyano-thiophen in furan led to the rapid disappearance of the reactant and the formation of two crystalline 1:1 adducts (5, 71%) and (6, 7%). The structures of the adducts were assigned primarily on the basis of their n.m.r. spectra, which resembled those of the analogous adducts obtained from cyanopyrroles,[5] and the desulphurisation of (5) with trimethyl phosphite to the known[5] tricyclic diene (7). The formation of (5) and (6), together with the virtually complete suppression of 2-cyanothiophen formation in furan, provide strong evidence for the intermediacy in the photo-transposition of the thiabicyclopentene (2), of which (5)

§ For the first four substrates in the Table, 3-cyano products predominated. 2- to 3-Cyano product ratios: ca. 5 and 25, respectively, for 3-cyano-4-methyl- and 3-cyano-2-methyl-thiophen as substrates; very large for 2-cyano-3-methyl- and 2-cyano-5-methyl-thiophen.
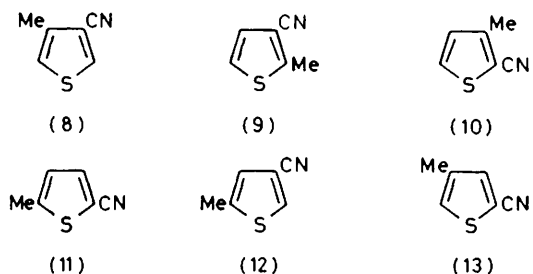
and (6) are the expected *endo* and *exo* Diels–Alder adducts with furan. 2-Cyanothiophen, irradiated in furan, gave the same adducts in similar proportions, but in reduced yield (18%). Analogous adducts were obtained from the methyl homologues.

Me—CN

(8)

CN / Me

(9)

Me / CN

(10)

Me / CN

(11)

Me / CN

(12)

Me / CN

(13)

Pyrolysis of (5) at 170 °C gave furan and a 1:1 mixture of 2- and 3-cyanothiophen. Presumably, the species (2) is regenerated under these conditions, and interconverts with its tautomer (1) faster than it rearomatises.

Cyanothiophens thus resemble cyanopyrroles[3,5] in photochemical behaviour, except that (i) double 'walks' (permutation **F**) are much more common in the thiophens, and (ii) pyrrole counterparts of the 2 → 2-, 3 → 2-, and 3 → 3-cyanothiophen conversions have not been observed. If the proposed mechanism is correct, these differences may imply that, under the reaction conditions, 'walking' of the heteroatom competes more effectively with rearomatisation in 5-thiabicyclo[2.1.0]pent-2-enes than in the corresponding 5-aza-compounds.

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