Photoinduced and Thermally Induced Rearrangements in a Thianthrenium Salt System

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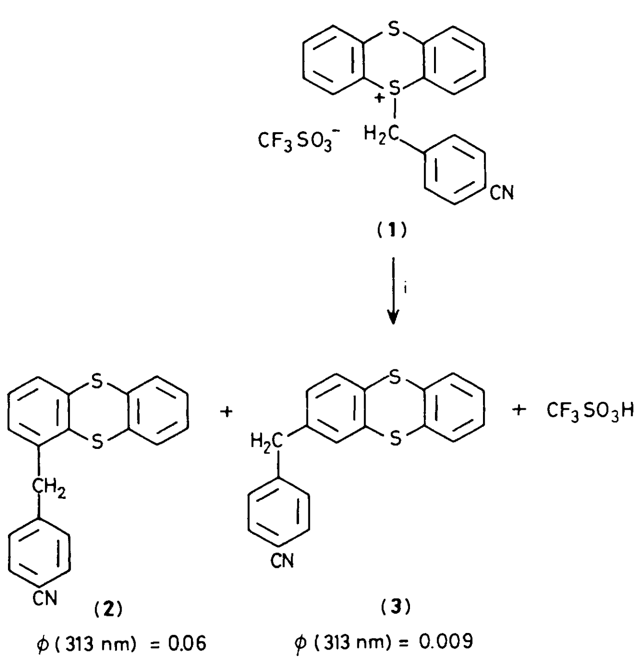
A low-lying σ^* level localized on a sulphur–carbon moiety in *p*-cyanobenzylthianthrenium trifluoromethanesulphonate allows facile photoinduced molecular rearrangements to occur *via* an in-cage fragmentation–recombination mechanism involving cation-radical–radical intermediates.

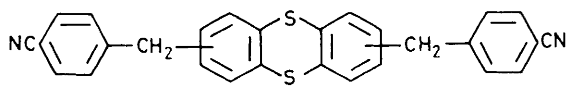
There is considerable interest in thermally and photochemically induced electron transfer between electron donors and electron acceptors, especially as it relates to the design of organic conductors[1,2] and photoconductors.[3] Most organic electron acceptors can be classified as π-acceptors, of which aromatic hydrocarbons are typical examples. There are, however, a few organic σ-acceptors such as alkyl halides[4] that show irreversible electrochemical reduction due to concerted electron acceptance and bond cleavage. This process would eliminate the possibility of reverse electron transfer back to an oxidized donor. It has been determined recently that the lowest unoccupied molecular orbital (LUMO) in phenyl and naphthyl dialkylsulphonium salts is the σ^* antibonding level of the sulphur–alkyl carbon bond, and that peak potentials for electrochemical reduction reflect the relative energy of this level.[5]

We now report that *p*-cyanobenzylthianthrenium trifluoromethanesulphonate (**1**) undergoes facile photorearrangement and thermal rearrangement, in which the benzyl group migrates from sulphur to the aryl ring, and participates in a variety of thermally initiated reactions.

The formation of (**3**) along with (**2**) as a result of photolysis of (**1**) (Scheme 1) is consistent with the formation of a thianthrene cation-radical–*p*-cyanobenzyl radical pair, which recombines either reversibly at sulphur or at the 1- or 2-position of the thianthrene cation-radical. The thianthrene cation-radical and *p*-cyanobenzyl radical have been postulated as intermediates in both the photochemical and thermal reaction in view of the following observations: (i) the appearance of the electronic absorption of the thianthrene cation radical in both the photochemical and thermal chemistry; (ii) the detection of trace quantities of derivatives of the *p*-cyanobenzyl radical; and (iii) the fact that related onium salts, which possess magnetically active heteroatoms such as phosphorus, nitrogen, and arsenic, photochemically produce mainly out-of-cage products derived directly from these intermediates, *e.g.*, phosphine oxide and the bibenzyl derivative.[6]



Scheme 1. *Reagents and conditions:* i, *h*ν >310 nm; MeCN.

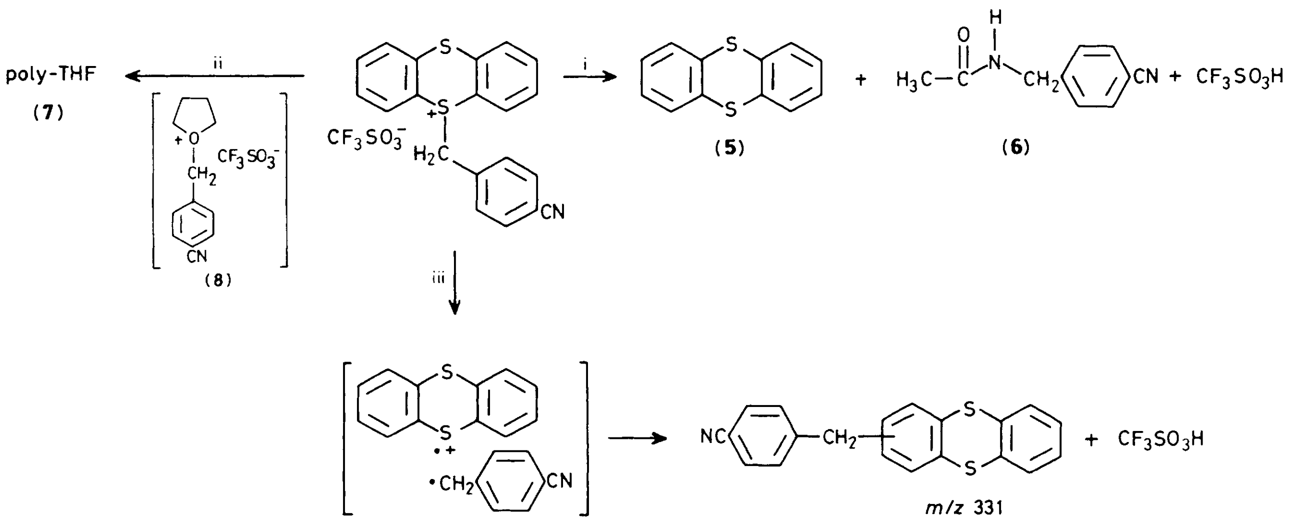


(**4**)
m/z 446

The product distribution does not reflect the spin densities within the cation-radical.[7] The 2,3- and 7,8-carbon atoms of the thianthrene cation radical were found experimentally by Shine[7] to possess considerably more spin density than the 1,4-carbon atoms.

Long photolysis produced small quantities (*ca.* 1%) of *p*-toluonitrile, presumably from hydrogen atom abstraction by the *p*-cyanobenzyl radical. When the photolysis was run in the presence and the absence of molecular oxygen, *i.e.*, purging with molecular oxygen or argon, respectively, no effect was observed on the product yield or the ratio of isomers. *p*-Cyanobenzaldehyde was detected in trace quantities (*ca.* 1%) in both the argon- and molecular oxygen-purged photolyses. When the photolysis was run in the presence of 1.0 M benzenethiol as a hydrogen atom source to quench radicals, both rearrangement products were formed in the same ratio as in the absence of the thiol but with a greatly reduced efficiency, owing to the involvement of ground-state chemistry. It appears that the radicals produced react faster, *i.e.*, react in-cage, to form products, than they diffuse out-of-cage.

Thermolysis of (**1**), as a solid, produced the thianthrene cation-radical, as indicated by the appearance of its characteristic electronic absorption at 136 °C.[8] The solid-state thermal behaviour of (**1**) was investigated by mass spectral analysis. Compound (**1**) gave species with the same *m/z* as the photoproducts within the probe of the mass spectrometer, and the study indicated that a species of *m/z* 446 was formed in substantial quantities. This species may be thianthrene containing two *p*-cyanobenzyl groups attached to carbon (**4**). The fate of the *p*-cyanobenzyl radical formed in the thermolysis reaction, other than that which couples with the thianthrene cation-radical, is not known. The bibenzyl derivative was not



Scheme 2. *Reagents and conditions:* i, MeCN, H_2O; ii, THF; iii, heat.

observed. This information supports the fragmentation–recombination mechanism for the thermal and photoinduced rearrangements.

The thermal chemistry appears to be governed by the fact that the sulphur–benzylic carbon bond is extremely weak and can be readily cleaved, both homolytically and heterolytically. The sulphonium salt (**1**) reacted in the dark with weak nucleophiles, *e.g.*, acetonitrile and tetrahydrofuran (THF) (Scheme 2). In acetonitrile solvent (1.0×10^{-2} M) at 36 °C, (**1**) gave thianthrene (**5**) and *p*-cyanobenzylacetamide (**6**) in 58% yield in 18 h. In THF, on the other hand (**1**) produced poly-THF (**7**) with $\bar{M}_n = 52\,000$, presumably through the benzyloxonium salt (**8**). The molecular weight distribution of (**7**) ($\bar{M}_w/\bar{M}_n$) was 1.96.

Photochemical excitation of an n (or π) electron from the highest occupied molecular orbital (HOMO) in (**1**) to the σ* LUMO level and thermal treatment of (**1**) appear to produce the same intermediates, a cation-radical–radical pair, which allow the observed rearrangement of a *p*-cyanobenzyl group from sulphur to the aromatic ring.

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