Rapid Migration of Sulphur Groups in the Photochemical Conversion of 3-Azido-2-vinylthiophenes into Thienopyrroles

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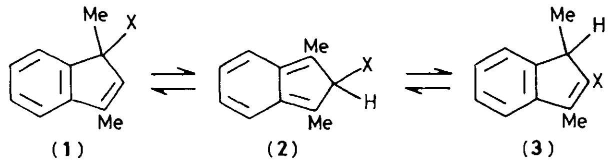
On irradiation in acetonitrile, the 3-azido-2-vinylthiophenes (**4**) give the thieno[3,2-*b*]pyrroles (**8**) as the sole, or major, products formed by migration of the group Y (Scheme 2) in preference to or in competition with the group Z in the non-aromatic fused 2*H*-pyrrole intermediate (**5**), sulphur groups (Y = PhS, MeS, PhSO, $PhSO_2$, MeSO, $MeSO_2$) migrating particularly rapidly.

Although the relative migratory aptitudes of a variety of carbon based groups in carbocyclic systems have been investigated, notably by Jones and co-workers (Scheme 1),[1] little is known about the sigmatropic migration of heteroatom groups.[2] The 1*H*-indene (**1**), when heated, may rearrange to the non-aromatic 2*H*-isomer (**2**) by a [1,5]-sigmatropic shift of the X-group.[1] If the X-group migrates faster than hydrogen then aromatisation reforms the 1*H*-isomer (**1**). However, if hydrogen is the faster migrator then the isomeric 1*H*-indene (**3**) is formed on rearomatisation. In a series of elegant experiments starting from optically active 1*H*-indenes (**1**), Jones determined the relative order of migratory aptitudes for a series of X-groups: alkyl < C≡CH < CN < CO_2Me < $CH{=}CH_2$ < H < COMe < CHO. We have previously inferred[3] that in 5,5-heterocyclic systems, isoelectronic with the 2*H*-indene (**2**), sulphur groups migrate particularly readily, and we now report results which confirm this.

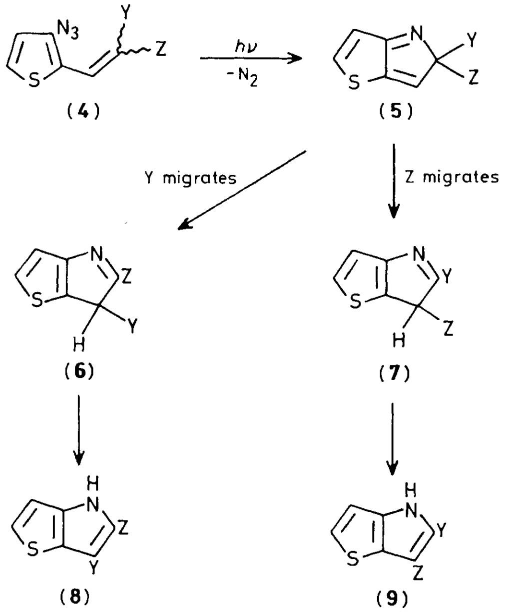
The starting materials for the investigation were the 3-azido-2-vinylthiophenes (**4**), readily prepared from 3-azidothiophene-2-carbaldehyde or 3-bromothiophene-2-carbaldehyde by standard methods. Irradiation of the azides (**4**) was expected to result in loss of nitrogen and collapse of the resulting nitrene to give the non-aromatic fused 2*H*-pyrrole (**5**). Since work on 2*H*-pyrroles has shown that substituents only migrate from carbon to nitrogen when all other positions are blocked,[4] rearomatisation of (**5**) is likely to occur *via* initial migration of Y (or Z) to give the 3*H*-pyrrole (**6**) or (**7**), followed by two successive 'dark' [1,5]-hydrogen shifts or a photochemical [1,3]-shift (Scheme 2). Therefore, a simple examination of the aromatic thieno[3,2-*b*]pyrrole products, (**8**) or (**9**), derived from each of the azides (**4**) would provide information on the relative ease of migration of Y *vs.* Z.

Irradiation of azides (**4a**) and (**4b**) in acetonitrile both gave single thienopyrrole products, the structures of which were established as (**8a**) (90%) and (**8b**) (90%).† Interestingly, azide (**4b**) also gives thienopyrrole (**8b**) on thermolysis.[5] The conversion of azides (**4c**) and (**4d**) into thienopyrroles (**8c**) and (**8d**) on irradiation has already been described,[3] and established the more rapid migration of both PhS and MeS groups over the ester. Increasing the oxidation level of the sulphur substituent has little effect, PhSO and $PhSO_2$ groups still migrating more readily than ester. Thus irradiation of the azides (**4e**) and (**4f**) gave the thienopyrroles (**8e**) (52%) and (**8f**) (80%) respectively. However, when two sulphur groups are compared directly, an effect of oxidation level is observed, the azide (**4g**) giving a single thienopyrrole (**8g**) (55%) derived by exclusive migration of the MeSO group.

In order to establish the relative ease of migration of various sulphur groups *vs.* hydrogen, azides (**4h**—**4j**) were irradiated. Azide (**4h**) gave both the thienopyrroles (**8h**) (27%) and (**9h**) (22%) in approximately equal amounts, together with much dark coloured polar material, demonstrating that migration of MeS competes effectively with hydrogen. As expected from the result with azide (**4g**), PhSO competed still more



Scheme 1



a; Y = COMe, Z = CO_2Et
b; Y = H, Z = COMe
c; Y = SPh, Z = CO_2Et
d; Y = SMe, Z = CO_2Et
e; Y = SOPh, Z = CO_2Et
f; Y = SO_2Ph, Z = CO_2Et
g; Y = SOMe, Z = SMe
h; Y = SMe, Z = H
i; Y = SOPh, Z = H
j; Y = H, Z = SO_2Me

Scheme 2

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† The structures of all the thienopyrrole products are supported by elemental analysis (or high resolution mass spectrometry), and full spectral data, including nuclear Overhauser effect difference experiments in their ^1H n.m.r. spectra. The ^1H n.m.r. spectra of the crude photolysates were recorded; when the formation of only one product is reported, there was no evidence of the other isomer. When both isomers were formed the spectra agreed with the ratio of the reported yields of isolated products.

effectively with migration of hydrogen, and azide (**4i**) gave the thienopyrroles (**8i**) (48%) and (**9i**) (26%) in the approximate ratio 2:1 on irradiation. In contrast, photolysis of sulphone (**4j**) gave only the thienopyrrole (**8j**) (86%), derived by exclusive hydrogen migration.

Therefore, photochemical decomposition of the 3-azido-2-vinylthiophenes (**4**) leads to thienopyrroles (**8**) formed by migration of the Y group in preference to or in competition with the Z group in the presumed non-aromatic fused 2*H*-pyrrole intermediate (**5**). For the groups studied the order of migratory aptitude is: $RSO > RS \sim H > RSO_2 > RCO > EtO_2C$.

The greater migratory aptitude of hydrogen over acetyl in the heterocyclic series is opposite to the results in the carbocyclic series,[1] but probably arises from a direct aromatising hydrogen shift to nitrogen in the 2*H*-pyrrole intermediate. The extra driving force of aromatisation of the five-membered ring is not applicable in the indene series. Although the exact details of the migration steps are not known, it is clear that sulphur groups migrate very rapidly, and the reasons for this merit further investigation.

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