Orbital Symmetry Control in the Rearrangements of Allylic Sulphonium Ylides

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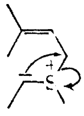
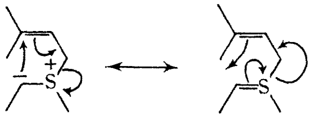
IN rearrangement reactions involving intermediate allylic sulphonium ylides,[1] two product-determining paths may be recognised, involving either a three-centred Stevens rearrangement (I) or a five-centred allylic rearrangement (II). These transformations could be either concerted reactions or equivalent unconcerted processes involving intimate or separated ion-pair intermediates. The base-catalysed reactions of a number of allylic sulphonium salts have been studied to examine factors which could influence competition between the two processes (IV) → (V) and (IV) → (VI).

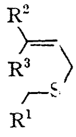
Reaction of α-toluenethiol with the allyl bromides ($CH_2{=}CH{\cdot}CH_2Br$, $Me_2C{=}CH{\cdot}CH_2Br$, and $PhCH{=}CH{\cdot}CH_2Br$) or alkylation of the corresponding allyl thiols with either *p*-nitrobenzyl bromide or phenacyl bromide gave the nine sulphides† (IIIa—j) which, with triethyloxonium tetrafluoroborate, gave the corresponding sulphonium tetrafluoroborates (IVa—j). Treatment of these sulphonium tetrafluoroborates (IVa—j) in alcoholic solution at room temperature with the indicated basic reagent [(IVa, b, d, g, h) (sodium ethoxide); (IVc, e, f, j) (anhydrous potassium carbonate)] gave the rearrangement products (Va—j) in high yield; no trace of the isomers (VIb, c, e, f, h, or j) could be detected in the reaction products.



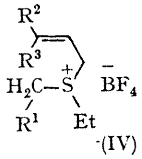
(I)



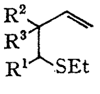
(IIa) (IIb)



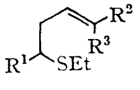
(III)



(IV)



(V)



(VI)

(a) $R^1{=}Ph$
(d) $R^1{=}p\text{-}O_2NC_6H_4$ } $R^2{=}R^3{=}H$
(g) $R^1{=}PhCO$

(b) $R^1{=}Ph$
(e) $R^1{=}p\text{-}O_2NC_6H_4$ } $R^2{=}R^3{=}Me$
(h) $R^1{=}PhCO$

(c) $R^1{=}Ph$
(f) $R^1{=}p\text{-}O_2NC_6H_4$ } $R^2{=}Ph$, $R^3{=}H$
(j) $R^1{=}PhCO$

Empirical extension of the Woodward–Hoffmann rules[2,3] in the sense in which they have been applied to allylic[4] and other sigmatropic rearrangements[5,6] leads to the recognition[7] that a concerted Stevens rearrangement (I) with retention of configuration at the terminus of the migrating group is symmetry-forbidden, whereas the five-centred allylic rearrangement (II) is symmetry-allowed. The alternative view that allowed sigmatropic reactions involve homoaromatic transition states[8] also leads to the opinion that the allylic rearrangement (II) with its bishomothiophen transition-state will be a thermally-allowed process. Thus, the exclusive course [(IV) → (V); (IV) ↛ (VI)] of these reactions is in accord with expectation for a concerted process. The concerted rearrangement has been formulated either as an internal nucleophilic displacement[7] (IIa) or as an electron reorganisation involving a tetracovalent sulphur intermediate[9] (IIb). The distinction between these processes [see arrows of (IIa) and (IIb)] disappears when it is recognised that the representations (IIa) and (IIb) (minus the arrows) are related as canonical forms.

The rearrangement of the benzyl sulphonium salt (IVc) gave a product (Vc) which was a mixture (*ca.* 40 : 60) of

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† All new compounds have been fully characterised by analysis and by their i.r., n.m.r., and mass spectra.

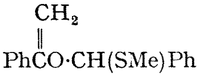
two diastereomeric racemates. The stereochemical consequences of the process (II) could reflect the stereoselective removal of the diastereotopic[10] hydrogen atoms of the indicated CH_2 group in formula (IV), and this opinion is related to the important proposals[11] recently made concerning *syn*- and *anti*-elimination reaction mechanisms.

$PhCO\cdot CH_2\overset{+}{S}(Me)\cdot CH_2Ph$

(VII)

$PhCO\cdot CH(SMe)\cdot CH_2Ph$

(VIII)



$PhCO(=CH_2)\cdot CH(SMe)Ph$

(IX)

$C_{12}H_{25}SO_2\cdot CH_2\cdot\overset{+}{S}Me_2$

(X)

$C_{12}H_{25}SO_2CH(Me)\cdot SMe$

(XI)

The exclusive rearrangement (IVj) → (Vj) should be compared with the base-catalysed rearrangement of the sulphonium bromide (VII). This reaction was initially formulated as giving the symmetry-forbidden Stevens rearrangement product[12] (VIII), but the product was later shown to be the isomeric ether[13] (IX) formed by a symmetry-allowed process.[7,9] Thus, of the four courses of reaction formally available to the ylide derived from the sulphonium salt (IVj), the product (Vj) is determined by the symmetry-allowed process (II) rather than the alternative symmetry-allowed process related to the reaction (VII → IX).

The rearrangement (X → XI) recently described[14] is formally symmetry-forbidden in the context of the present investigation.

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