

## Simultaneous Observation of a Radical Pathway and Retention in a Stevens Rearrangement of a Sulphonium Ylide: Significance for a General Theory of Ylide Rearrangements

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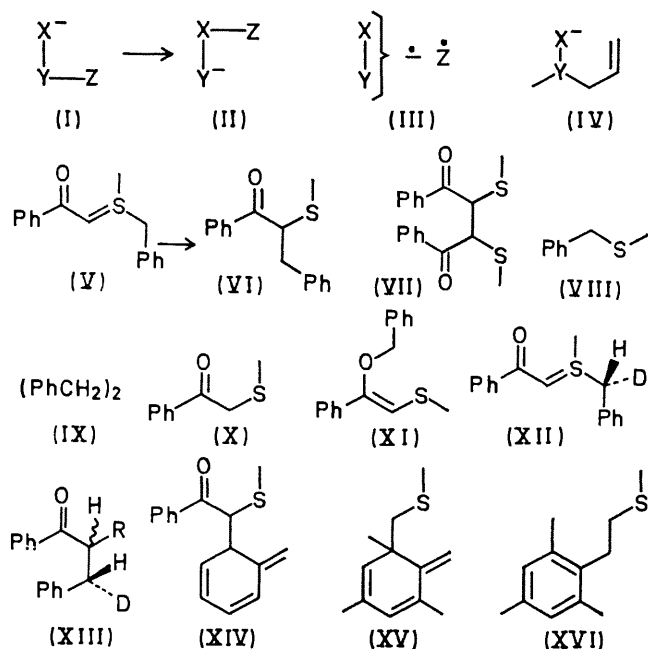
**Summary** The chiral ylide (V) undergoes a thermal Stevens rearrangement by a radical pathway in which 36% of the stereochemical integrity of the migrating site is preserved and during the course of which process chemically induced dynamic nuclear polarization (CIDNP) effects are observed for the protons at the migrating group: a determination of the extent of the cage effect in this system has been made, which eliminates a radical chain process as the major pathway.

THE mechanism of 1,2-rearrangements of the general type (I) to (II)<sup>1</sup> has caused considerable speculation, especially since the observations of retention of configuration in the

migrating residue Z.<sup>2</sup> The concerted front-side displacement<sup>3</sup> cannot proceed with retention of orbital symmetry and it has been suggested that if these are concerted processes perhaps metal ions may play a part in the mechanism.<sup>4</sup> We now report observations, in a system free of metal ions, most readily interpreted by the postulation of an intermediate radical pair (III). These observations are in accord with our earlier studies of system (IV)<sup>5</sup> which demonstrated the simultaneous operation of a concerted [3,2]-sigmatropic pathway and the radical dissociation-recombination process.

The stable ylide (V)<sup>6</sup> was converted into (VI)—(XI) (Table), along with traces of acetophenone and benzoic

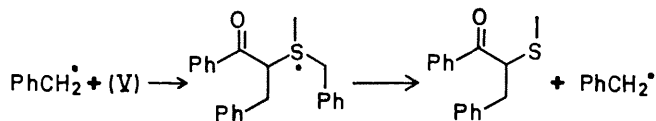
acid,<sup>†</sup> within 5 min in refluxing toluene, the major product (VI) being the result of a Stevens rearrangement. When this pyrolysis was carried out in diphenyl ether at 130° CIDNP<sup>7</sup> was observed in the methine proton of (VI) (enhanced absorption; maximum being 35 relative to final absorption, enhancement for 30 s) and in the methylene protons (emission; enhancement 20; for 30 s). The same effects, but predictably simplified to a singlet and double doublet, were observed in compounds with deuteriated



methylene and methine groups, respectively. A CIDNP effect in (VI) has already been briefly noted<sup>8</sup> and it is now evident that the observation of abnormal proton polarizations at the point of bond formation is indicative of paramagnetic precursors, in this case the pair (III). In order to evaluate the extent to which the initially formed radicals in (III) are independent we performed a crossover experiment. Thus an intimate mixture of the dideuterio-(V) (labelled in the benzylic protons) and the pentadeuterio-species (V) (labelled in the phenacyl ring) was rearranged at 130° (neat). The isotopic content of the Stevens product (VI) was consistent only with 18 ± 6% being formed by escape from the primary radical pair and subsequent recombination. Therefore, a radical chain process (Scheme) is not the major pathway involved in the generation of Stevens product.

To assess the degree of stereochemical integrity maintained in the primary radical pair (III) the chiral ylide (XII) was prepared and rearranged under identical conditions in refluxing toluene. Stereospecific monodeuteration of (*S*)-benzyl methyl sulphoxide and reduction gave (*R*)-benzyl methyl sulphide,  $[\alpha]_D^{25} - 1.12 \pm 0.01^\circ$  (*c* 18, EtOH) of 73% optical purity.<sup>9</sup> Conversion into the ylide (XII) was achieved in the usual manner and subsequent reduction with zinc-acetic acid back to (*R*)-benzyl methyl sulphide,  $[\alpha]_D^{25} - 1.02 \pm 0.12^\circ$  (*c* 2, EtOH) demonstrated

that the ylide was still at least 58% optically pure (precision 66 ± 7%). Rearrangement of the chiral ylide (XII) provided the diastereoisomeric Stevens product (XIII; R = SMe) which was reduced with zinc in acetic acid to the monodeuteriated ketone (XIII; R = H)  $[\alpha]_D^{25} + 0.14 \pm 0.03^\circ$  (*c* 3, CHCl<sub>3</sub>). The absence of prior stereochemical data on this substance required its preparation: this was achieved by displacement of  $\alpha$ -methylthioacetophenone on (*R*)-(-)- $\alpha$ -deuteriobenzyl alcohol tosylate



SCHEME

of known optical purity (47%) followed by reduction, to the enantiomer of (XIII; R = H),  $[\alpha]_D^{25} - 0.28 \pm 0.02$  (*c* 6, CHCl<sub>3</sub>). Assuming complete inversion in this displacement<sup>10</sup> it is possible to calculate the optical purity (24 ± 7%) of the (*S*)-(+)-deuteriopropiophenone (XIII; R = H) derived from the Stevens product. Thus from the measured optical purity of the ylide (66 ± 7%) the rearrangement to Stevens product proceeded with a net retention of 36 ± 15%. The actual degree of retention in that portion of the product (82 ± 6%), *vide supra*, which remains within the cage is then 44 ± 20%, since those fragments escaping from the primary cage almost certainly are completely racemised.

An alternative mechanism for the formation of Stevens product (VI) involves a prior concerted [3,2]-sigmatropic rearrangement<sup>11</sup> to the nonbenzenoid intermediate (XIV) which would then homolyse and recombine as we have shown in earlier work on the nitrogen system.<sup>12</sup> That this is a possibility was shown by the observation of a CIDNP effect at the benzylic protons (A<sub>2</sub>B<sub>2</sub> system) in the thermal (170°) isomerisation of the sulphide (XV) to the aromatic isomer (XVI). However, recent work has shown that carbonyl stabilised nitrogen ylides do not rearrange by a combination of sigmatropic and dissociative mechanisms,<sup>13</sup> but directly undergo homolysis and recombination. It seems reasonable to expect this tendency to operate within the stabilised sulphur systems also.

TABLE

Product <sup>a</sup>	(VI)	(VII)	(VIII)	(IX)	(X)	(XI)
Yield (mole %) <sup>b</sup>	45	22	17	14	9	5

<sup>a</sup> All new compounds have satisfactory analytical and spectral data.

<sup>b</sup> Based on parts of the starting material, and hence total >100%. These compounds, with the traces of autoxidation products, account for 98% of the SMe, 85% of the CO, and 80% of the CH<sub>2</sub> fragments.

We have observed simultaneously CIDNP and retention of stereochemistry in a Stevens rearrangement of a sulphonium ylide in which the product is only formed to a minor extent by intermolecular mechanisms. This evidence is in accord with the earlier postulations of radical pairs in this rearrangement of sulphonium ylides,<sup>5</sup> and taken in conjunction with work reported from other laboratories

† Shown to result from autoxidation of the ylide.

suggests that the mechanism of isoelectronic rearrangements, described by (I) to (II), proceeds through the radical pair (III). In this group are to be found the Stevens rearrangement of ammonium ylides (I,  $X = \bar{C}^{\ominus}$ ,  $Y = \bar{N}^{\oplus}$ ,  $Z = C \equiv$ ),<sup>14</sup> the Wittig rearrangement (I,  $X = \bar{C}^{\ominus}$ ,  $Y = O$ ,  $Z = C \equiv$ ),<sup>15</sup> the Meisenheimer rearrangement (I,  $X = \bar{O}$ ,  $Y = \bar{N}^{\oplus}$ ,  $Z = C \equiv$ ),<sup>16</sup> the Zimmerman-Grovenstein reaction (I,  $X = \bar{C}^{\ominus}$ ,  $Y = C =$ ,  $Z = C \equiv$ ),<sup>17</sup> the rearrangement of sulphenates (I,  $X = S^-$ ,  $Y = O$ ,  $Z = C \equiv$ ),<sup>18</sup> and

the thermal rearrangement of ammonio-amidates (I,  $X = \bar{N}^{\ominus}$ ,  $Y = \bar{N}^{\oplus}$ ,  $Z = C \equiv$ )<sup>13,19</sup>. In systems (IV), which contain a further pair of electrons, as a double bond, the concerted, symmetry conserved, [2,3]-sigmatropic reaction predominates in most structural environments.

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