Skeletal Rearrangement of [1-^{13}C]Diphenyl Sulphide on Electron Impact[1]

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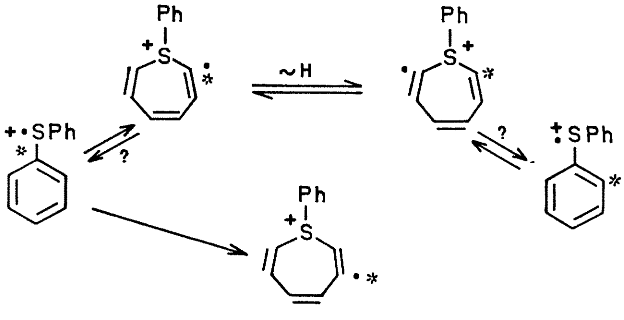
Summary [1-^{13}C]Diphenyl sulphide eliminates CS and related fragments on electron impact after scrambling of the substituent group with respect to the phenyl rings.

SKELETAL rearrangements on electron impact of a number of aromatic compounds with the general formula PhX have been reported recently[2] where the substituent X is bound to a benzene ring *via* an atom other than carbon. In many of the cases investigated,[2c–d] including that of diphenyl sulphide,[2b] rearrangement is accompanied by extensive scrambling of the aromatic hydrogen atoms. Hydrogen scrambling has also been observed in the decomposition of a number of other atomatic compounds including benzene and pyridine,[4] and it appears to be a common reaction of gaseous aromatic ions. We present some results of our study of skeletal rearrangements in diphenyl sulphide which elucidate the mechanism by which hydrogen scrambling occurs in this compound.

Hydrogen scrambling in compounds PhX can occur by two different types of mechanism. In mechanisms of type A, the hydrogen atoms are scrambled with respect to each other and to the substituent, but the substituent itself remains bonded to its original ring carbon atom. In mechanisms of type B, both the hydrogen atoms and the substituent group are scrambled with respect to each other and the carbon atoms of the benzene ring. The two types of mechanism are distinguishable in the case of diphenyl sulphide by an analysis of the mass spectrum of its [1-^{13}C]-derivative. Diphenyl sulphide eliminates the fragments CS, CHS, CH_2S, and CH_3S on electron impact; assuming that the C–S bond in the intermediates retains its identity in the fragments, then hydrogen scrambling and skeletal rearrangement by mechanisms of type A would result in the loss of 50% of the ^{13}C label, while the operation of mechanisms of type B would result in the loss of between 50 and 8·3% of the label, depending on the extent of scrambling.

[1-^{13}C]Diphenyl sulphide was prepared from [1-^{13}C]-aniline[5] *via* the labelled phenyl diazonium chloride, and was purified by preparative-scale g.l.p.c. Analysis of the low-voltage mass spectrum of the molecular ion region indicated that the sample contained 49·7% ^{13}C after correction for natural abundance ^{13}C. Intensities of peaks in the mass range of 139—143 for the low-resolution mass spectrum of both labelled and unlabelled material at 70 ev and at 20 ev are given in the Table. The figures in columns 4 and 6 were calculated from the data for the unlabelled material by adjusting the various parameters until a best fit was obtained between the observed and calculated data. The calculated retention of ^{13}C label is relatively insensitive to the exact values obtained for the individual ion intensities; best fit values were obtained for a mean label retention of 82% (81% for the M — CHS ion) at 70 ev, and 87% (84% for the M — CHS ion) at 20 ev.

These results clearly support a mechanism of type B for the rearrangement and hydrogen scrambling of diphenyl sulphide. The fact that label loss (18% at 70 ev and 13% at 20 ev) is greater than would be predicted for complete scrambling by mechanisms of this type could be due to incomplete randomization prior to fragmentation; alternatively, the simultaneous operation of a scrambling mechanism of type A† cannot be excluded. Possible type B mechanisms include those proceeding through ring-expanded intermediates (Scheme 1), through episulphide intermediates (Scheme 2), or through a series of reversible reactions involving the formation of σ- and π-complexes of the substituent.[7] Mechanisms involving ring-expanded



SCHEME 1‡

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† Possible type A mechanisms include those involving reversible formation of benzvalene or prismane isomers of the aromatic compound (ref. 6) and those involving the reversible formation of σ- or π-complexes between the aromatic ring and its hydrogen atoms (ref. 7). It would seem to be necessary to postulate a mechanism of this type to explain hydrogen scrambling in benzene (ref. 3), pyridine (ref. 4), and similar compounds.

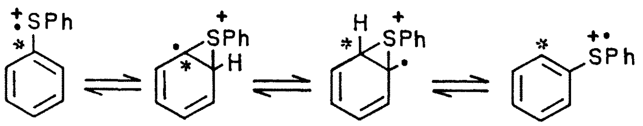
‡ Possible routes for scrambling include insertion of the sulphur atom as indicated into other than an adjacent ring position, and hydrogen migration in the seven-membered ring followed by ring contraction to a new six-membered-ring isomer.

Mass spectral peaks for [1-^{13}C]*diphenyl sulphide*

m/e	Ion	Relative abundance, 70 ev[a–e]		Relative abundance, 20 ev[a–e]	
		Observed	Calculated[f]	Observed	Calculated[g]
143	$^{13}CC_{10}H_{10}$	0·086	0·093	0·197	0·193
142	$^{13}CC_{10}H_9 + C_{11}H_{10}$	0·271 (0·208)	0·279	0·464 (0·433)	0·460
141	$^{13}CC_{10}H_8 + C_{11}H_9$	0·268 (0·432)	0·260	0·307 (0·513)	0·307
140	$^{13}CC_{10}H_7 + C_{11}H_8$	0·162 (0·024)	0·155	0·024 (0·011)	0·024
139	$C_{11}H_7$	0·213 (0·336)	0·206	0·008 (0·043)	0·020

[a] $\Sigma_{139-143} = 1{\cdot}000$. [b] Corrected for naturally abundant ^{13}C. [c] Values in parentheses are for unlabelled diphenyl sulphide, corrected for natural ^{13}C. [d] Average of at least 5 scans. [e] Measured on an AE1/GEC MS-902 mass spectrometer. [f] Values correspond to 82% mean retention of ^{13}C label. [g] Values correspond to 87% mean retention of ^{13}C label.

intermediates are the most attractive in view of the recent evidence that both toluene[8] and probably also aniline[9] rearrange *via* such intermediates.



SCHEME 2

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