1,3-Proton Transfer in Dimethyl Sulphoxide without Hydrogen Exchange with the Solvent

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Summary 3-Phenylpropyne, phenylallene, and 3-phenylprop-1-ene undergo in Me_2SO a methylsulphinyl carbanion-catalysed isomerization with very little H–D exchange with the solvent.

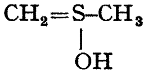
BASE-CATALYSED rearrangements of acetylenes[1] were shown to proceed from a low (18%) to high (85%) intramolecularity.[2] Similar variations in base-catalysed intramolecular 1,3- and 1,5-proton or deuteron transfer were observed also in the isomerization of olefins.[2–8] This intramolecularity was rationalized by hydrogen-bond formation between the proton donor and the electron cloud of the intermediate carbanion. The amount of intramolecularity was found to be low in Me_2SO when a charged base was used as catalyst, and high when uncharged bases such as tertiary amines or non-dissociating solvents were used for the reaction.[2,7,9] When a secondary or primary amine was substituted for the tertiary amine, intramolecularity dropped almost to the statistical value corresponding to the number of protons on the nitrogen.[2,9]

We have found that isomerization of 3-phenylpropyne to phenylallene in $(CD_3)_2SO$ solution using [$^2H_5$]methylsulphinyl carbanion[10] as a catalyst proceeded in more than 90% without hydrogen–deuterium exchange with the solvent (analysis by n.m.r.). This could be proved by integration and the pattern of the spectrum, which showed a triplet for the hydrogen on the carbon next to the phenyl group. This 1,3-transfer was not caused by sodium hydroxide catalysis, since independent experiments have shown the sodium hydroxide-catalysed reaction to be considerably slower.

This intramolecular transfer was unexpected, since Me_2SO is a dissociating solvent. Moreover, abstraction of the propargylic proton by the methylsulphinyl carbanion should give the propargylic-allenic anion and a neutral molecule of [$^2H_5$]Me_2SO. Me_2SO is not known to form hydrogen bonds and even assuming the formation of such a bond, rotation of the [$^2H_5$]Me_2SO molecule formed should produce exchange as in the case of the primary and secondary amine-catalysed reactions.[2,9]

The methylsulphinyl carbanion-catalysed isomerization of [1,3,3-$^2H_3$]-3-phenylpropyne in Me_2SO proceeded also with intramolecularity similar to that of 3-phenylpropyne. This result eliminated the possibility that the isotope effect was responsible in that case for the observed intramolecularity.

There are two possible explanations for the observed effect: (i) abstraction of a proton by methylsulphinyl carbanion gives a tautomer (I) of Me_2SO which is acidic and hydrogen-bonded to the anion formed.

(I) 

$$CH_2{=}\underset{\displaystyle OH}{\underset{|}{S}}{-}CH_3$$

Protonation of this anion proceeded according to this hypothesis almost exclusively by the OH group of (I). (ii) Another possibility is protonation of the anion by another molecule of phenylpropyne and not by Me_2SO. Proton transfers from a carbon acid to its conjugate base or to a conjugate base of a related carbon acid were shown recently to be faster than from Me_2SO to these bases.[11] This second hypothesis seems to us to be more probable at present, since there is, to our knowledge, no other evidence for the formation of (I). The [$^2H_5$]methylsulphinyl carbanion-catalysed isomerization of phenylallene to 1-phenylpropyne proceeds in more than 95% without intervention of the solvent. However, under these conditions, the 1-phenylpropyne begins to exchange the methyl protons soon after its formation.

It is also of interest that allylbenzene is isomerized under the same conditions to 1-phenylpropene with only 20% exchange with the solvent. This is a smaller amount of exchange than in the potassium t-butoxide in Bu^{t}OD-catalysed reaction, where more than 40% of exchange was observed. *A priori* prediction would be of more exchange in Me_2SO solution, but a competition between direct transfer of protons from the unsaturated compound to its conjugate base and from the solvent to the base can explain the result in Me_2SO.

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