Orientation in Elimination from Carbanions

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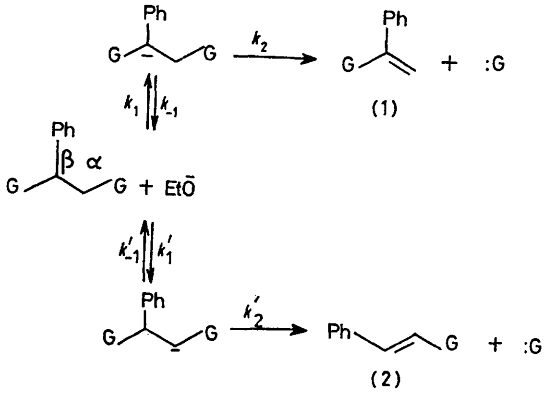
Summary Orientation in 1,2-elimination from a carbanion in 1,2-bis-sulphides and phosphonates is directed by a phenyl group to give the alkene derived by the more rapid deprotonation at the site of phenyl substitution;

the opposite orientation of elimination in bis-sulphones is due to steric repression of deprotonation.

ACTIVATION of alkene-forming elimination by carbanion-stabilising groups, G, allows study of a wide range of leaving groups.[1] Some groups such as $PhSO_2$, PhS, and $(EtO)_2PO$ activate carbanionic elimination but also can be expelled as the leaving group, so that elimination in symmetrical substrates GCH_2CH_2G can occur. We report on the striking effect of phenyl substitution in such systems.

The reactivity of three substrates of the type $GCHPhCH_2G$ with ethanolic sodium ethoxide is summarised in the Table. All eliminate by the $(E_1cB)_R$ mechanism ($k_{\text{detritiation}} > k_{\text{elimination}}$) in which loss of the leaving group is rate determining. The rate constant for elimination is thus $k_{\text{obs}} = k_1k_2/k_{-1}[\text{BH}] + k_2$.



SCHEME

TABLE. Effect of phenyl substitution on orientation and reactivity in elimination from carbanions.

Substrate	k_{obs}[a]/l mol^{-1} s^{-1}	$k^{\text{obs}}_{\text{rel}}$ β-Ph : H[b]	$k^{\beta}_{\text{detrit.}}$[a]/l mol^{-1} s^{-1}	$k^{\alpha}_{\text{detrit.}}$[a]/l mol^{-1} s^{-1}	Alkene/% (1)	Alkene/% (2)
(3)[c]	1.03×10^{-4}	121	2.3×10^{-2}	2.6×10^{-4}	98	d
(4)	9.3×10^{-2}	1.3×10^{6}	1.2×10^{1}	4.0×10^{-2}	97[f]	d
(5)	38.8	37.0	8.5×10^{-6}[g]	1.6×10^{-4}[g]	3.3[f]	96.1

[a] Reactions with EtONa–EtOH at 25 °C. [b] Value for unsubstituted substate statistically corrected. [c] Reactions at 95 °C. [d] None detected. [e] Extrapolated ratio; reaction with unsubstituted substrate at 95 °C. [f] As ethoxy adduct. [g] Base Et_3N, conversion factor 1.7×10^5.

Insertion of a phenyl group accelerates elimination in all substrates and, when G = SPh or $(EtO)_2PO$, overwhelmingly directs orientation to give the alkene (**1**) (Scheme). In the bis-sulphone $PhSO_2CHPh{\cdot}CH_2SO_2Ph$ (**5**), phenyl substitution slightly accelerates elimination but this is now almost entirely in the opposite direction to give the alkene (**2**).

Detritiation measurements (Table) show that it is the effect of the phenyl group on deprotonation (k_1) that determines orientation. The bis-sulphide PhSCHPh-CH_2SPh (**3**) and the bis-phosphonate $(EtO)_2P(O)CHPh$-$CH_2P(O)(OEt)_2$ (**4**) lose tritium very much more rapidly from the phenyl-bearing site. In the bis-sulphone (**5**) the co-planar arrangement of ligands required for optimum stabilisation of the carbanion is obviated. Deprotonation, which initiates elimination, occurs preferentially from the other site.

The effect of phenyl substitution on the k_2/k_1 ratio could also affect orientation. We have recently shown, however, that *differential* effects of α- and β-phenyl substitution on this ratio in a substantial number of substrates are small.[2]

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[1] D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, *J.C.S. Perkin II*, 1978, 1898.

[2] R. P. Redman, P. J. Thomas, and C. J. M. Stirling, *J.C.S. Perkin II*, 1978, 1135.