Intramolecular Alkylation of Phenoxide Ions

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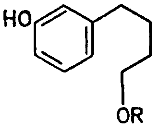
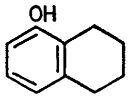
Summary A new base-catalysed cyclisation (Ar_2^--6) involves phenyl participation; *O*-alkylation is inhibited by dilution, and the *ortho–para*-alkylation ratio is solvent dependent.

BOTH the mechanistic[1] and synthetic[2] aspects of phenyl participation in displacement reactions have been investigated. However, no information was available from these studies on the factors which influence the *ortho–para*-alkylation ratio of phenoxide ions, since investigation of the Ar_2^- mechanism was limited to *para*-substituted phenoxides.[1] The generalisation has been made that *ortho*-alkylation of phenoxide ions is favoured in displacement reactions[3] and *para*-alkylation is preferred by carbonium ions.[3a,4] However, the detailed mechanism of reactions between these two extremes remains unclear, most especially under homogeneous conditions.[3b,5]

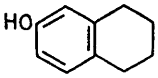
We now report an example of the hitherto unreported Ar$_2^-$ mechanism. Thus, a solution (10^{-3}M) of the sulphonate (I) in anhydrous t-butyl alcohol–tetrahydrofuran (50:10), cyclised within 10 h under reflux, with a slight excess of potassium t-butoxide, to give (II) (75%) and (III) (25%)† Initial *O*-alkylation followed by rearrangement[4b,6] to (II) or (III) was excluded by g.l.c. and t.l.c. Phenyl participation during the reaction was further indicated since the benzyl ether of (I) did not react under the same conditions as did (I).‡



(I) R=*p*-MeC$_6$H$_4$SO$_2$
(IV) R=H



(II)



(III)

The relatively high proportion of *para*-alkylation is exceptional.[4b] This orientation has been noted previously only with allyl halides,[3b] with alkylating agents such as diphenylmethyl or triphenylmethyl halides,[4] or when the *ortho*-positions are substituted.[4b,7] As observed by others,[7] *ortho*-alkylation is facilitated by ion-paired metal cations.§ In a dissociating solvent a decrease in the percentage of the *ortho*-isomer (II) might therefore be expected. In boiling water with KOH (5 mol. equiv.) (I) reacted to give a combined yield of 88% of (II) and (III) (38:62), and 12% of (IV).† That the Ar$_2^-$ mechanism persisted under these conditions is indicated by the predominance of solvolysis in the reaction of (I) in boiling water in the absence of a base. Combined yields of 25% of (II) and (III) (38:62) and 75% (IV) were obtained.†

Although *para*-alkylation of phenoxide ions may be preferred by carbonium ions,[4] our results suggest that attack at this position is not 'diagnostic of the intermediacy of carbonium ions.[3a]

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† A small quantity of *O*-alkylated product was also detected. This will be described in the full paper.

‡ Compared at 30°.

§ Evidence for ion-pair formation in Bu^{t}OH–THF is based on a metal cation effect on the *ortho–para* ratio Li$^+$: 87% (II), 13% (III); Na$^+$: 85% (II), 15% (III); K$^+$: 75% (II), 25% (III).

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