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COMPETITIVE C-O AND S-O CLEAVAGE MECHANISMS IN REACTION OF ALKYL ALKANESULFONATES WITH ARENE ANION RADICALS[1]

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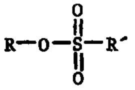
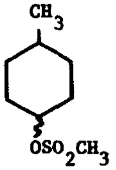
As previously noted, alkyl alkanesulfonates, unlike the corresponding tosylates, do not give good yields of the corresponding alcohols on treatment with sodium naphthalene.[3] Instead, mixtures of alcohol and the corresponding alkane are obtained. We wish to present evidence bearing on the mechanism of cleavage of this class of compounds.

In a typical reaction, where a dilute (0.04 M) solution of octadecyl butanesulfonate (Ia)[4] is injected rapidly into an excess of 0.2 M sodium naphthalene in THF at 25°, one obtains a 44% yield of alcohol and 20% of octadecane, and an amount of naphthalene corresponding to about 30% of Ia is converted to high boiling material (presumably alkylated dihydronaphthalenes). This production of both alkane and alkylated naphthalenes is characteristic of production of alkyl radicals in the presence of naphthalene anion radical.[5] Radical production must be relatively slow, however, since no products of dimerization are detected (e.g., no n-octane

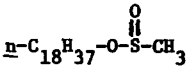


$\mathrm{R{-}O{-}\overset{O}{\underset{O}{S}}{-}R'}$

Ia, R=n-$C_{18}H_{37}$, R′=n-butyl
b, R=n-butyl, R′=CH_3
c, R=2-phenylethyl, R′=CH_3
d, R=neopentyl, R′= CH_3



II, a = cis
b = trans



$n\text{-}C_{18}H_{37}\text{-}O\text{-}\overset{O}{\underset{}{S}}\text{-}CH_3$

III

from n-butyl methanesulfonate, Ib), contrary to the reaction of alkyl iodides and bromides with sodium naphthalene.[6] From similar cleavage of alkyl methanesulfonates, both methanesulfinate and methanesulfonate ions could be identified among the water soluble products.[7]

A simple competition between C-O and S-O cleavage concerted with, or immediately following, electron transfer, (eq. 1), is ruled out by the often striking sensitivity of the product mix to arene anion radical concentration. Thus, when Ia is injected rapidly into an excess of 0.06 M sodium naphthalene at 25° 17% octadecanol and 19% octadecane re obtained; with conditions identical except for increasing anion radical concentration to 0.25 M, 36% alcohol and 17% alkane are obtained. If 1 mmole of 2-phenylethyl methanesulfonate (Ic) is added slowly to 1 M sodium naphthalene a 37% yield of alcohol is obtained; if a dilute solution of Ic is treated slowly with 0.1 M sodium naphthalene only about 2% alcohol is formed. For neopentyl methanesulfonate (Id), yields of 49% and ca. 5% alcohol result using the two methods of mixing, respectively. The increase in production of alkoxide with increasing anion radical

$$\mathrm{ROSO_2R' + Naph^{\dot{-}}} \begin{cases} \longrightarrow \mathrm{R^{\cdot} + R'SO_3^{-} + Naph} \\ \longrightarrow \mathrm{RO^{-/\cdot} + R'SO_2^{\,\cdot/-} + Naph} \end{cases} \tag{1}$$

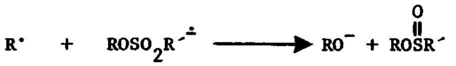
concentration leads us to postulate eq. 2-4 as the most likely reaction sequence, with step 4 competing rather well with step 3 at high anion radical concentrations. An alternative

$$\mathrm{ROSO_2R' + Naph^{\dot{-}}} \;\overset{\longrightarrow}{(\longleftarrow)}\; \mathrm{ROSO_2R'^{\dot{-}} + Naph} \tag{2}$$

$$\mathrm{ROSO_2R'^{\dot{-}}} \xrightarrow{\qquad\quad} \mathrm{R^{\cdot} + R'SO_3^{-}} \tag{3}$$

$$\mathrm{ROSO_2R^{\dot{-}} + Naph^{\dot{-}}} \longrightarrow \longrightarrow \mathrm{RO^{-} + R'SO_2^{-} + Naph} \tag{4}$$

mechanism for production of alkoxide, illustrated in eq. 5, similar to addition of alkyl radicals to nitroalkane anion radicals[8] is ruled out by the fact that methanesulfonates II a and II b



$$\mathrm{R^{\cdot} + ROSO_2R'^{\dot{-}}} \longrightarrow \mathrm{RO^{-} + RO\overset{\overset{O}{\|}}{S}R'} \tag{5}$$

yield on treatment with sodium naphthalene only cis-(24%) and trans-4-methylcyclohexanol (45%), respectively, in addition to methylcyclohexane. Retention of stereochemistry is unlikely if the precursor to alkoxide is the 4-methylcyclohexyl radical. Furthermore, operation of eq. 5 would require that the resulting alkanesulfinate ester undergo at least largely C–O cleavage in order to account for formation of the observed methanesulfinate ion. Treatment of octadecyl methanesulfinate (III) with sodium naphthalene yields only *n*-octadecanol, however, implying S-O cleavage for sulfinate esters. Finally, a second alternative for production of alkoxide is illustrated in eq. 6. A certain amount of α-carbanion of the sulfonate ester could readily

$$\mathrm{R{-}OSO_2{-}\bar{C}}\!< \;+\; \mathrm{Naph}^{\dot{-}} \longrightarrow \mathrm{RO}^{-} \;+\; >\!\mathrm{\bar{C}{-}SO_2}^{\cdot} \;+\; \mathrm{Naph} \qquad (6)$$

be formed in these reactions, considering the known acidity of α-protons of sulfonate esters[9] and that strong bases such as alkyl and alkyldihydronaphthyl carbanions are generated. However, treatment of Id with an excess of either sodium hydride or *n*-butyl lithium (either of which converts Id at least largely to its α-carbanion),[9c] followed by dilute sodium naphthalene, failed to result in an increase in yield of alcohol (*ca*. 2% observed). In fact, a considerable amount of Id (30-50%) could be recovered from these reaction mixtures in spite of 30 min. contact with sodium naphthalene at 25°. (Survival of the α-carbanion of Id would be expected if its reaction with sodium naphthalene were slow. Other alkanesulfonate carbanions could more easily undergo self alkylation[9d] and then react as neutral esters.) Significant amounts of Id can often be recovered after reaction of the neutral ester.

In summation, most of the evidence points toward the combination of steps 2, 3, and 4 as the most likely cleavage mechanism. Reactions of alkyl alkanesulfonates with the anion radicals of biphenyl and phenanthrene apparently also proceed in a similar manner. With sodium anthracene, however, only α-proton abstraction, and apparent SN2 reaction leading to alkylated anthracenes, takes place.[10]

REFERENCES

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4. All compounds used either had physical properties agreeing with literature values or gave correct C and H analyses. The m.p.'s of new compounds were: Ia, 37.5-38°; III, 37-39°.

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7. Analysis by nmr using sodium acetate as internal standard. In D_2O methanesulfinate ion has a singlet at -25 Hz relative to the acetate peak while methanesulfonate ion comes at -56 Hz relative to acetate.

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10. Neopentyl alkanesulfonates apparently only protonate sodium anthracene, and are recovered quantitatively after quenching the reaction mixture with water, implying that alkylation of anthracene anion radical is probably straightforward SN2 in nature.