Coplanar *vs.* Orthogonal Bimolecular Substitution at a Benzylic Carbon

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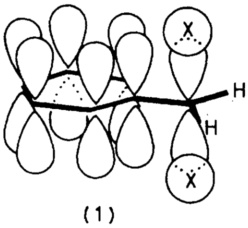
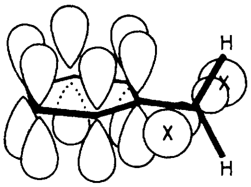
Summary Bimolecular substitution at the benzylic centre in dibenzylethylsulphonium fluoroborate (**8**) with thiocyanate anion is 8000 times faster than the corresponding reaction in the cyclic sulphonium fluoroborate (**4**) in which the attacking and leaving groups must remain in approximately the plane of the benzene ring thereby precluding conjugation in the transition state; it is estimated that a *ca.* thousand-fold increase in rate is attributable to conjugation in unconstrained benzylic substitution.

IT has been known for many years that bimolecular nucleophilic substitution occurs at a benzylic centre with notable ease,[1] a phenomenon ascribed[2] to stabilization of the transition state by conjugation with the aromatic ring as shown in (**1**). Theory predicts that such conjugation will be greatest in the 'orthogonal' arrangement† shown in (**1**), and will diminish to zero in the 'coplanar' form (**2**), *i.e.* as the dihedral angle, θ, as defined in (**3**) varies from 90 to 0°. There would appear, however, to be no direct experimental information relating the rate of bimolecular nucleophilic substitution to the dihedral angle, θ. As the first step in providing such information, we now report our study of a 'coplanar' benzylic S_N2 reaction.



(1)



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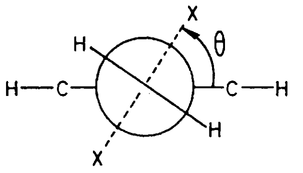

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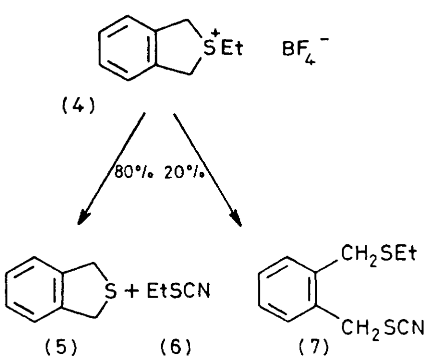
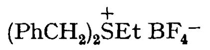


SCHEME. Reaction medium: KSCN, 18-crown-6, CD_3CN.

The cyclic sulphonium salt (**4**) is readily prepared by reaction of dihydroisothianaphthene (**5**) with triethyloxonium fluoroborate, and reacts cleanly with potassium thiocyanate and 18-crown-6 in CD_3CN to give a mixture containing chiefly (80%) dihydroisothianaphthene (**5**) with an equivalent amount of ethyl thiocyanate (**6**), and a minor amount (20%) of the sulphide-thiocyanate (**7**), as shown in the Scheme. By contrast, similar reaction of dibenzylethylsulphonium fluoroborate (**8**) gave benzyl ethyl sulphide and benzyl thiocyanate, but no dibenzyl sulphide or ethyl thiocyanate. Control experiments showed that dibenzyl sulphide, ethyl thiocyanate, and the products from both (**4**) and (**8**) are stable to the reaction conditions; we infer that the product ratios give a direct measure of the rate constant ratios. The rates of disappearance of (**4**), (**8**), and (**9**) were followed by an n.m.r. method, and the observed second order rate constants together with derived values for the specific rate of attack at one benzyl or ethyl position in the appropriate substrate are given in the Table. It is evident that the specific rate of attack at one benzylic centre (k_{Bz}) in (**8**) is 8 × 10³ times greater than that in (**4**). Since the benzyl groups in (**8**) are free to adopt the orthogonal conformation (**1**) in the transition state whereas in (**4**) the transition state must be constrained to something close to the coplanar arrangement (**2**), these results are clearly in agreement with the idea of conjugation in the transition state.[2]



$(PhCH_2)_2\overset{+}{S}Et\ BF_4^-$

(**8**)

$Et_3\overset{+}{S}\ BF_4^-$

(**9**)

TABLE.

Substrate	T/°C	Rate constant/l mol⁻¹ s⁻¹ k_{obs}	k_{Et}[a]	k_{Bz}[a]
(**4**)	37·0	$4{\cdot}8\times10^{-6}$	$3{\cdot}8\times10^{-6}$	$4{\cdot}8\times10^{-7}$
(**4**)	59·0	$1{\cdot}0\times10^{-4}$	$0{\cdot}8\times10^{-4}$	$0{\cdot}1\times10^{-4}$
(**8**)	37·0	8×10^{-3}	—	4×10^{-3}
(**9**)	59·0	$2{\cdot}5\times10^{-5}$	$0{\cdot}8\times10^{-5}$	—

[a] Bz = benzyl. Values of k_{Et} and k_{Bz} were obtained from k_{obs} by (where appropriate) (a) multiplying by the fraction of the product of the corresponding reaction, and (b) dividing by the appropriate statistical factor; *e.g.* k_{Bz} for compound (**4**) is given by k_{obs} × [%(**7**)/100] ÷ 2.

These observations establish experimentally that an approximately coplanar substitution is much slower than the orthogonal reaction at a benzylic centre. Also desirable would be a quantitative assessment of the factors controlling such orthogonal and coplanar substitutions relative to a

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† 'Coplanar' and 'orthogonal' describe relationships of nuclei, *viz.* of the plane of the benzylic system on the one hand and the (ideally straight) line joining the nucleophile, the carbon undergoing substitution, and the leaving group, on the other.

standard substitution. For the present case we chose as our standard the substitution at one ethyl group[2a] in triethylsulphonium fluoroborate (**9**), and suggest that the following are the major factors: (i) the stereoelectronic effect (f_{SE}), *i.e.* conjugation as in (**1**), described above, (ii) a ring strain effect (f_{RS}) in the opening of the five-membered ring in (**4**), and (iii) a non-bonding repulsion effect (f_{NB}) deriving primarily from the interaction in (**2**) between the nucleophile and the nearby *ortho* hydrogen atom. If we assume that the effect of these factors may simply be multiplied,[3] and label the specific rates for orthogonal benzylic, coplanar benzylic, and ethyl substitutions as k_{OB}, k_{CB}, and k_{Et}, and the factors for each of these effects as f_{SE}, f_{RS}, and $_{NB}$ as indicated above, we obtain equation (1).

$$k_{OB}/k_{CB} = f_{SE}/f_{RS}f_{NB} = 8 \times 10^3 \qquad (1)$$

From the ratio of (**7**) to (**5**) in the products from (**4**), taken with a statistical correction for the two benzylic groups we get equation (2), which on substitution into equation (1)

$$k_{CB}/k_{Et} = f_{RS}f_{NB} = 1/8 \qquad (2)$$

gives us $f_{SE} = 10^3$; *i.e.* the effect of conjugation in orthogonal benzylic substitution is to increase the rate by roughly a thousand-fold.‡ The existence of the ring-strain effect (f_{RS}) is highly likely in the light of the observations of Eliel *et al.*[5] on the relative tendencies of five- and six-membered ring saturated methylsulphonium salts to undergo ring cleavage in the presence of a nucleophile. They found that relative to attack at the methyl group, ring opening was *ca.* 25 times more favoured in the five-membered than in the six-membered ring, and assigned this difference to relief of strain accompanying opening of the five-membered ring. If there is comparable ring strain in (**4**), then from equation (2) an f_{RS} value *ca.* 25 would lead to a non-bonding repulsion factor, f_{NB}, of about 0·005, a not unreasonable number in the light of other steric effects on S_N2 reactions.§

We thank the Natural Sciences and Engineering Research Council of Canada for support of this work.

(*Received*, 29*th August* 1979; *Com.* 912.)

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‡ More detailed analysis might also include (a) a term to account for the difference in k_{Et} between (**4**) and (**9**), and (b) possible polar (as distinguished from resonance) effects in benzylic substitution.[4] Available information suggests that these effects are not large and approximately cancel each other.

§ The 'typical' relative rates[2a] for the series ethyl, propyl, isobutyl, neopentyl (1·0, 0·4, 0·03, 10^{-5}) are regarded[2a,6] as arising primarily from non-bonding repulsions. Another instance clearly ascribable to such interactions is the 20- to 30-fold slower S_N2 reaction of an axial CH_2X grouping *vs.* its equatorial analogue.[7]

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