repulsive interactions with neighboring groups in the molecule.[10]

[10] H. J. Bernstein and W. G. Schneider, *J. Chem. Phys.*, **24**, 468 (1956), have just published NSR data for aromatic condensed ring systems. "Anomalous" peak displacements toward lesser shielding, inconsistent with molecular-orbital predictions but in accord with the concept of "repulsive unshielding," were found for the hydrogen atoms at the 4,5-positions of phenanthrene and at similar hindered positions in more complex molecules. For biphenyl the repulsive interaction of these hydrogen atoms results in deviations from coplanarity; *cf.* G. W. Wheland, "Resonance in Organic Chemistry," Wiley, N. Y., 1955, pp. 157–162.

CONTRIBUTION NO. 107, CENTRAL RESEARCH DEPARTMENT
MINNESOTA MINING AND MANUFACTURING COMPANY
ST. PAUL 6, MINNESOTA GEORGE VAN DYKE TIERS

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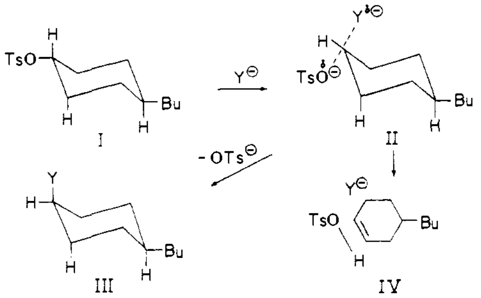
MERGED BIMOLECULAR SUBSTITUTION AND ELIMINATION[1]

Sir:

While elimination accompanying bimolecular nucleophilic substitution (SN2) of alkyl halides or toluenesulfonates is not well recognized in the case of relatively non-basic nucleophiles such as halide ion, we have occasionally observed such elimination, and several pertinent examples are available in the literature.[2] Mechanistically, the behavior of *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate (I), which has the toluenesulfonoxy group constrained to an *equatorial* position,[3] is instructive.



With lithium bromide in acetone at 75°, I undergoes a second order reaction, partly substitution and partly elimination to 4-*t*-butylcyclohexene (IV). The behavior of the *cis*-4-*t*-butylcyclohexyl *p*-toluenesulfonate is analogous, the total reaction rate and the fraction of elimination, *F*E, being *ca.* 7 and *ca.* 2 times as large, respectively.

Considering possible elimination mechanisms for I, the E2 mechanism is essentially precluded by stereoelectronic considerations.[3] The sequence of SN2 followed by E2 does not account for the observed elimination, since the intermediate bromide proves to be too unreactive by a factor of at least 10^2. An E1 elimination mechanism involving ionization of I, promoted by lithium bromide but without nucleophilic attack by bromide ion, is precluded by a substantial rate factor between lithium bromide and lithium perchlorate. On the other hand, lithium perchlorate gives rise to reaction rates as high or higher than does lithium bromide with *exo*-norbornyl, *p*-methoxyneophyl and pinacolyl benzenesulfonates, substances disposed toward ionization without nucleophilic attack by an external nucleophile.

It is suggested that nucleophilic attack of halide ion on I gives rise to an actual intermediate II, with the electronic and geometrical structure generally ascribed to the transition state in SN2 substitution. From this intermediate is obtained substitution product III by loss of OTs^- and also olefin IV, the latter by a process which disengages a β-proton and both the incoming and outgoing nucleophiles, Y^- and OTs^-. Stereoelectronic considerations[3] suggest that preferably an *axial* proton is lost. While a solvent molecule may remove the proton, the leaving group OTs^- appears also to be in a position to depart with the proton, and this is the manner in which the formation of olefin is represented in formulas II–IV. On the basis of this mechanism, *F*E would be expected to decrease with ascending nucleophilicity of the anion Y^-, as is actually observed and summarized in Table I for the series of halide and thiophenolate[4] ions. The identity of *F*E (0.25 ± 0.01) for both $(n\text{-}C_4H_9)_4N^+Br^-$ and Li^+Br^- also supports the suggested mechanism rather than some form of cyclic *cis*-elimination mechanism.[2b]

TABLE I

SUBSTITUTION AND ELIMINATION OF THE 4-*t*-BUTYLCYCLOHEXYL TOLUENESULFONATES IN ACETONE AT 75°

			*F*E	
Salt	Rel. rate[a]	*n*[b]	*trans* ROTs	*cis* ROTs
LiCl	1	3.04	0.30	
Bu_4NBr	10	3.89	.25	
LiBr	5	3.89	.25	0.57
NaI	5	5.04	*ca.* .10	.41
$NaSC_6H_5$[c,4]		High	*ca.* 0	.48

[a] Total second order rate. [b] Nucleophilic constants of the anions [C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953)]. [c] In 90% EtOH at 25°.

While the scope of the present mechanism for elimination is not yet clear, it should further our understanding of certain *cis*- or non-stereospecific eliminations and certain competitions between substitution and elimination. The proposed mechanism need not be restricted to cases of elimination of HX, and it can be generalized to elimination of ZX, where Z is also halogen, etc.

DEPARTMENT OF CHEMISTRY S. WINSTEIN
UNIVERSITY OF CALIFORNIA D. DARWISH
LOS ANGELES 24, CALIFORNIA N. J. HOLNESS

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[2] (a) A. L. Solomon and H. C. Thomas, THIS JOURNAL, **72**, 2028 (1950); (b) R. P. Holysz, *ibid.*, **75**, 4432 (1953); (c) D. J. Cram and F. A. Elhafez, *ibid.*, **76**, 28 (1954).

[3] S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

[4] E. L. Eliel and R. S. Ro, *Chemistry and Industry*, 251 (1956).