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NOTES

An example of merged bimolecular substitution and elimination

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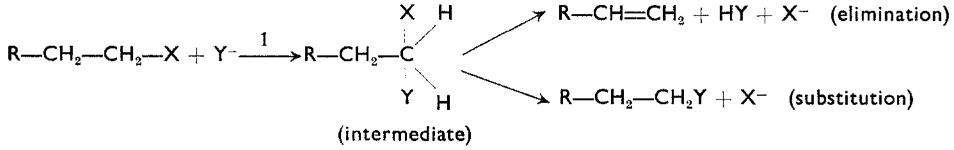
WINSTEIN, DARWISH and HOLNESS[1] have recently postulated the existence of a new mechanism of simultaneous S_N2 and E_2 reactions which they call "merged bimolecular substitution and elimination". The mechanism may be schematized as follows:



Presumably formation of the intermediate (step 1) is rate-determining.

In an investigation which we are undertaking with different ends in mind, we have found evidence in support of the merged mechanism. When 4,4-dimethyl*cyclo*hexyl tosylate (I) was treated with sodium thiophenolate in 87% ethanol and the reaction followed acidimetrically, an overall second-order rate constant ($k_s + k_e$) of 19·04 (all rate constants given in l. mole^{-1} sec^{-1} $\times 10^5$) was found. Iodimetric titration during reaction indicated that the entire* rate was due to substitution, i.e. $k_s = 19{\cdot}04$ and $k_e = 0$. This result should be contrasted with one for the parent compound *cyclo*hexyl tosylate (II) where the reaction with thiophenolate proceeded at an overall specific rate $k_s + k_e$ of 18·35, of which however only part was substitution ($k_s = 10{\cdot}09$) and part was elimination ($k_e = 8{\cdot}26$).[2] The agreement of the overall rate constants ($k_s + k_e$) was at first sight reasonable, since I and II exist at about the same equilibrium mixture of equatorial and axial conformations (with respect to the tosylate grouping) (Fig. 1) and the feebly electron-donating methyl groups should have no appreciable polar affect at the remote 4-position of the ring.[3,4]† The difference in the individual rate constants k_s and k_e is, however, at first sight surprising. One can perhaps understand why elimination in I is slower than in II, since in I the axial hydrogens at C_2 are shielded from attack by base by the axial methyl at C_4. Indeed, we have found that the rate of bimolecular elimination for I with sodium ethoxide in absolute ethanol (0·349) is less than that for II (0·570) and the difference is magnified for the more bulky[5] base potassium *t*-butoxide in *t*-butanol (0·310 vs. 0·823). As thiophenolate may well

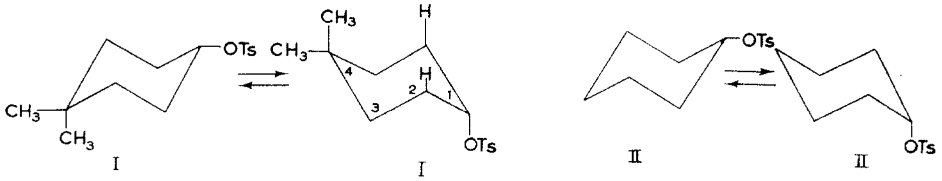


FIG. 1.

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* The accuracy of the method is such that if more than 5–10 per cent of the total reaction had been elimination, it would have been detected.

† *Cyclo*hexanol and 4,4-dimethyl*cyclo*hexanol are acetylated at the same rate with acetic anhydride in pyridine.

[1] S. Winstein, D. Darwish and N. J. Holness *J. Amer. Chem. Soc.* **78**, 2915 (1956).

[2] E. L. Eliel and R. S. Ro *Chem. & Ind.* (*Rev.*) 251 (1956); *J. Amer. Chem. Soc.* **79**, 5995 (1957).

[3] J. F. J. Dippy, S. R. C. Hughes and J. W. Laxton *J. Chem. Soc.* 4102 (1954).

[4] E. L. Eliel and C. A. Lukach *J. Amer. Chem. Soc.* **79**, 5986 (1957).

[5] H. C. Brown and I. Moritani *J. Amer. Chem. Soc.* **75**, 4112 (1953); H. C. Brown, I. Moritani and Y. Okamoto *Ibid.* **78**, 2193 (1956).

have an even larger steric requirement than *t*-butoxide, the very slow elimination rate of I with this base is explained. It is not clear, however on the basis of the classical[6] S_N2-E_2 dichotomy why the *decrease* in elimination rate for I should lead to a corresponding *increase* in substitution rate so as to keep the overall rate approximately the same as for *cyclo*hexyl tosylate. On the basis of the merged mechanism[1] the interpretation is clear: The rate determining step 1 (equation above) proceeds at the same rate for I and II, but whereas the intermediate from II is converted partly to elimination and partly to substitution product, the intermediate from I gives substitution product exclusively (or nearly so) since elimination is sterically prevented. It is implied in this view that the product determining step in the merged mechanism involves attack by external base in so far as formation of the elimination product is concerned.

The merged mechanism implies that the rate-determining and product-determining steps are discrete. There are many instances in which this is not the case,[6] hence the merged mechanism cannot be general. It has been implied,[1] (and the present results seem to support this) that the merged mechanism is likely to be observed with strong nucleophiles of feebly basic properties, such as bromide and thiophenolate. The operation of the merged mechanism may be responsible for the remarkably high elimination rates observed in the reaction of *cyclo*hexyl tosylate,[2] *cis*-4-*t*-butyl*cyclo*hexyl tosylate[2] and *t*-butyl chloride[7] with sodium thiophenolate.

The present results are in good agreement with those obtained in the reaction of $(CH_3)_2CDCHOTsCH_3$ with bromide ion by Winstein *et al.*[8]

EXPERIMENTAL*

4,4-*Dimethyl*cyclo*hexyl tosylate* prepared from the parent alcohol[4] by the method of Tipson,[9] was a liquid purified by low-temperature crystallization.

Anal. Found: C, 63·93; H, 8·33; S, 11·36. $C_{15}H_{22}O_3S$ requires C, 63·80; H, 7·85; S, 11·35 per cent.

Kinetic measurements were performed as described elsewhere.[2]

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* Analysis by Micro-Tech Laboratories, Skokie, Illinois.

† Texas Company Fellow, 1954–1956.

[6] C. K. Ingold *Structure and Mechanism in Organic Chemistry* Chaps. VII and VIII. Cornell University Press, Ithaca, N. Y. (1953).

[7] P. B. D. de la Mare and C. A. Vernon *J. Chem. Soc.* 41 (1956).

[8] S. Winstein, D. Darwish and J. Takahashi Private communication.

[9] R. S. Tipson *J. Org. Chem.* **9**, 235 (1944).

Resonance energies of two unusually stable hydrocarbon free radicals

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THE radical α, γ-bisdiphenylene-β-phenylallyl (I) was first prepared by Koelsch in 1932.[1] Its stability is such that it reacts only slowly with molecular oxygen,[1,2] but electron spin resonance (ESR) measurements[2] have completely confirmed its radical nature.[2] In benzene solution I shows 1·1 radicals per mole by comparison of the integrated intensity of its ESR spectrum with that of diphenylpicrylhydrazyl.[2] The pentaphenyl*cyclo*pentadienyl radical (IV) is also reported[3] to be much more stable than the triphenylmethyl radical toward reaction with molecular oxygen and toward dimerization, although it does not appear to be quite as stable as I.[4] The present note reports that the great stability of I and IV toward reaction with molecular oxygen and toward dimerization is completely accountable on the basis of their resonance energies, as calculated by the simple L.C.A.O.M.O. method.[5]

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[1] C. F. Koelsch *J. Amer. Chem. Soc.* **79**, 4439 (1957).

[2] J. E. Wertz and J. L. Vivo Acrivos Unpublished results.

[3] K. Ziegler and B. Schnell *Liebigs Ann.* **445**, 266 (1925).

[4] J. Wertz Unpublished results.

[5] A. J. Streitwieser *J. Amer. Chem. Soc.* **74**, 5288 (1952). This paper contains very similar calculations and further references.