of greatest significance.[7] The lowest energy level at which this unique d orbital geometry is available is with principal quantum number 3.[8]

Specifically, it appears to us that fluorine and chlorine can differ in their ability to undergo a pi-type bonding (*e.g.*, $(2p\pi)_A-(3d\pi)_X$ overlap in A–X) which is not diagnosed with atomic optical excitation energies. More generally, we conclude that the higher valence states of all second row non-metals and their ability to accept electrons over the octet can continue to be logically interpreted as manifestations of d orbital utilization unavailable to first row elements.

(7) For example, resonance stabilization of an adjacent carbanion which is asymmetric is an ability of sulfur which would appear to uniquely require d orbital geometry; for a leading reference, see D. J. Cram, D. A. Scott and W. D. Nielsen, *J. Am. Chem. Soc.*, **83**, 3702 (1961).

(8) The possibility of utilizing 4d, 5d, *etc.*, character should also be considered, although in general the radii of orbitals of principal quantum number 4 and up are too great to allow useful overlap integrals in pi bonding to the relatively small atoms of the first two rows. However, it is possible to estimate a significant overlap integral specifically for $3d\pi$ of chlorine with $2p\pi$ of oxygen; see D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

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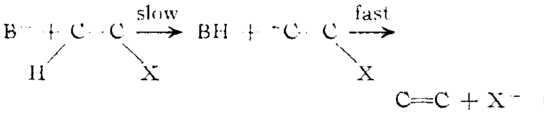
CONCERTED BIMOLECULAR ELIMINATIONS AND SOME COMMENTS ON THE EFFECT OF DIHEDRAL ANGLE ON E2 REACTIONS

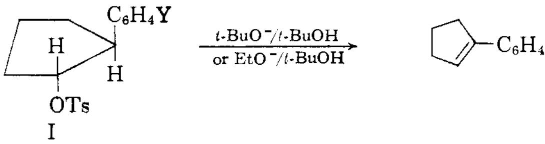
Sir:

Base-promoted elimination reactions are known to prefer transition states in which the departing groups (designated H and X) are *trans* to one another. Occasionally it is not possible for the molecule to assume such a transition state. In the cases studied, elimination then becomes very difficult.[1] In a classic case, Cristol[2] showed that the β-isomer of hexachlorocyclohexane, in which there are no *trans* hydrogens and chlorines, reacted $^1/_{7,000}$ to $^1/_{24,000}$ as fast as the other isomers. In this and other cases it has been proposed that *cis* eliminations, when they occurred, would substantially be E1CB reactions, involving complete or almost complete removal of the hydrogen, followed by a subsequent fast elimination (Eq. 1).



$$B^- + \underset{H}{C}-\underset{X}{C} \xrightarrow{\text{slow}} BH + {}^-C-\underset{X}{C} \xrightarrow{\text{fast}} C{=}C + X^- \quad (1)$$

We wish to report the first examples of a rapid concerted base-promoted *cis* elimination and the results of a kinetic study of these interesting reactions. A series of *trans*-2-arylcyclopentanols were prepared, both by reaction of cyclopentene oxide with aryllithium compounds and by reaction of 1-arylcyclopentene with diborane. The tosylates of these compounds underwent solvolysis reactions in ethyl alcohol, but readily reacted with bases in *tert*-butyl alcohol solution. The reactions were cleanly second order and the 1-arylcyclopentene was the sole product (Eq. 2), as shown by ultraviolet analysis of aliquots of the reaction mixtures.



I

(2)

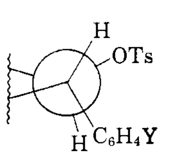
RATE CONSTANTS FOR THE REACTION OF I WITH POTASSIUM *t*-BUTOXIDE IN *t*-BUTYL ALCOHOL AT 46.8°

Y	$k \times 10^3$ (l. mole^{-1} sec.$^{-1}$)
p-CH_3	0.05
H	0.13
p-Cl	0.48
m-Cl	1.03

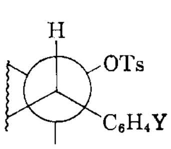
These data fit a Hammett[3,4] plot extremely well, giving $\rho = 2.34 \pm 0.03$. *Under the same conditions a series of β-arylethyl tosylates had $\rho = 3.39 \pm 0.29$.*[5] Clearly this *cis* elimination involves an even smaller amount of carbanionic character on the benzyl carbon, and the elimination is not E1CB.

cis-2-Phenylcyclopentanol was prepared by reduction of 2-phenylcyclopentanone. Its tosylate also underwent a base-promoted E2 reaction, this time a *trans* elimination. The rate constant for this elimination was 1.6×10^{-3} l./mole-sec. so that the *k-trans/k-cis is only 14 in the arylcyclopentyl system. Under identical conditions trans-2-phenylcyclohexyl tosylate failed to react after 22 days while cis-2-phenylcyclohexyl tosylate reacted rapidly. Hence in the cyclohexyl system k-trans/k-cis > 10^4.*

These results, taken in conjunction with a few previously discovered *cis* eliminations, have led us to some generalizations about the effect of dihedral angle, ϕ, on the rates of base-promoted eliminations. Since *cis* and *trans* coplanar eliminations both appear relatively favorable, while non-coplanar eliminations are slow, we suggest that a plot of the rate of elimination *vs.* the dihedral angle, ϕ, between hydrogen and the departing anion will show maxima at both 0° and 180° and a minimum at 90°.[6] This will reflect the fact that coplanar transition states, whether *cis* or *trans*, are vastly preferable to non-coplanar ones, insofar as concerted eliminations are concerned. Thus, a *cis* elimination in the cyclopentyl system could easily be coplanar while this would not be the case for *cis* eliminations from cyclohexyl compounds.



Cyclopentyl *cis* elimination



Cyclohexyl *cis* elimination

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(1) This is so unless the hydrogen being attacked is activated by a powerful electron-withdrawing group. In these special cases *cis* E2 reactions can be rapid.

(2) S. J. Cristol, N. L. Hause and J. S. Meck, *J. Am. Chem. Soc.*, **73**, 674 (1951).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184.

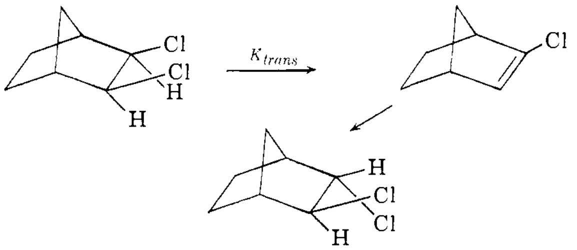
(4) H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

(5) C. H. DePuy and C. A. Bishop, *J. Am. Chem. Soc.*, **82**, 2532 (1960).

(6) It is of interest to note that the proposed plot for elimination reactions has the same general shape as that proposed by M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959), for the variation of n.m.r. coupling constants with dihedral angle, ϕ, for hydrogens on adjacent carbons. Whether there will be any general relationship between n.m.r. coupling constants and rates of elimination remains to be demonstrated.

Further evidence for the concerted elimination may be derived from the ρ of the reaction, a low value (< 4) being associated with a *more concerted* elimination. As a corollary to this, one might predict that as the dihedral angle approached 90° from either 0 or 180°, the elimination would approach E1CB and that ρ for the reaction would increase. These predictions are currently being tested.

Using the above predictions, certain results reported in the literature become more meaningful. Cristol and Hoegger[7] have reported that *cis* is faster than *trans* elimination in the bicycloheptyl system.



Obviously, a coplanar transition state is readily available for *cis* elimination but very difficult for *trans* elimination. Further evidence in support of these predictions is derived from the study of 11,12-dichloro-9,10-ethanoanthracene by Cristol and Hause.[8] In this system *k-cis/k-trans* is about 8 and again it can be seen that for *cis* elimination a coplanar transition state can occur, whereas such a state is impossible (or nearly so) for *trans* elimination.

[7] S. J. Cristol and E. F. Hoegger, *J. Am. Chem. Soc.*, **79**, 3438 (1957).

[8] S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952).

[9] Alfred P. Sloan Fellow.

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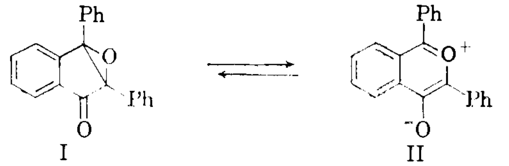
RECEIVED JANUARY 13, 1962

REVERSIBLE VALENCE TAUTOMERIZATION OF AN AROMATIC SYSTEM

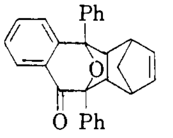
Sir:

While tropones have been observed to undergo light-induced valence tautomerizations,[1] no other aromatic compound has yet been converted to a valence tautomeric form.[2] We wish to report a remarkably facile equilibrium between the aromatic 1,3-diphenyl-2-benzopyrylium-4-oxide (II) and its valence tautomer, 2,3-diphenylindenone oxide (I).

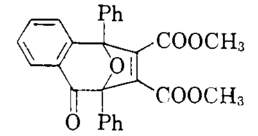


I II

Although the latter compound has long been known to be thermochromic,[3] the exact nature of this phenomenon has not been investigated. In agreement with the earlier observations, solutions of I were found to become red on heating to 80–100°, and to fade on standing at room temperature. In addition, it was found that the disappearance of the red color (λ_{max} 538 mμ in CH_3CN) was greatly accelerated by the addition of a variety of reagents including mineral acids, alkalies, bromine or oxygen. Significantly, the red color was destroyed instantaneously with bicyclo[2.2.1]-heptadiene or dimethyl acetylenedicarboxylate, reagents known to be highly reactive toward dipolar ions.[4] Indeed, after heating at 135–145° for four hours, solutions of I in these reagents were converted in good yields to the 1:1-adducts, III, m.p. 214–215°, and IV, m.p. 170–171°, respectively.[5]

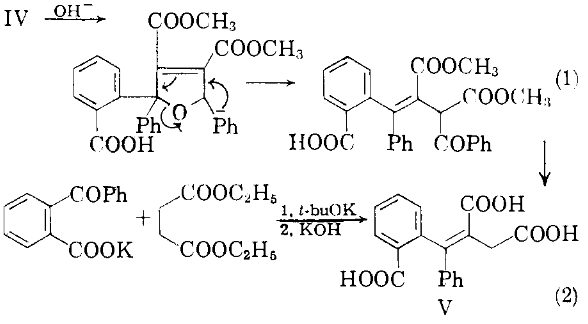


III



IV

The structures of these compounds were supported both by the shifts of the infrared carbonyl peaks (Nujol mulls) of III (5.89 μ) and dihydro-IV (5.87 μ) from that of I (5.78 μ), and by the close similarity of the ultraviolet spectra of III and dihydro-IV to that of tetralone. Compelling evidence for structure IV ultimately was obtained by treatment of IV with hot alcoholic alkali which led to the isolation of a $C_{18}H_{14}O_6$ tricarboxylic acid and benzoic acid. The new compound had a n.m.r. spectrum which showed a 9:2 ratio of aromatic (multiplet, 2.06–2.95τ) to aliphatic (singlet, 6.77τ) protons and an ultraviolet spectrum generally similar to that of *o*-carboxycinnamic acid. These data were in accord with the structure V expected upon consideration of the probable degradative sequence 1. Proof of structure V was obtained by comparison with an authentic sample synthesized by an application of the Stobbe condensation in which diethyl succinate was condensed directly with potassium *o*-benzoylbenzoate[6] (sequence 2).



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[1] E. J. Forbes, *J. Chem. Soc.*, 3864 (1955); O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **80**, 6685 (1958); **82**, 3642 (1960).

[2] The only report of such an isomerization, E. C. Taylor, W. W. Paudler and I. Kuntz, Jr., *ibid.*, **83**, 2967 (1961), was subsequently found to be incorrect, E. C. Taylor, R. O. Kan and W. W. Paudler, *ibid.*, **83**, 4484 (1961).

[3] E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

[4] R. Huisgen, R. Grashey, P. Lauer and H. Leitermann, *Angew. Chem.*, **72**, 416 (1960); R. Huisgen, H. Stangl, H. J. Sturm and H. Wagenhofer, *ibid.*, **73**, 170 (1961).

[5] All new compounds described herein have satisfactory carbon and hydrogen analyses.

[6] Use of the free salt rather than the ester of an *o*-ketobenzoic acid to prevent phthalide formation in the Stobbe condensation has been successfully employed previously, E. F. Ullman, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1956.