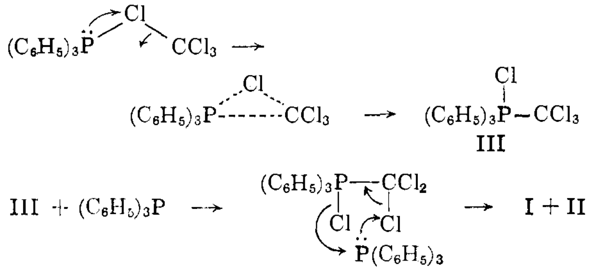
The reactions of other polyhalomethanes with triphenylphosphine in the presence of benzaldehyde have been investigated in a preliminary manner. Thus with bromotrichloromethane, β,β-dichlorostyrene was observed, and with dichlorodifluoromethane and dibromodifluoromethane, β,β-difluorostyrene was noted. When the system tributylphosphine–carbon tetrachloride–benzaldehyde was studied, small amounts of benzal chloride and β,β-chlorostyrene were observed. A detailed examination of the above reactions and related systems is now under way.

Although insufficient data has been accumulated to delineate a detailed mechanism, certain experimental facts must be accommodated.

The reaction proceeds readily in total darkness and is not accelerated by azobisisobutyronitrile at 60° or by ultraviolet light at room temperature. Further, when the reaction was carried out in the presence of tetramethylethylene *none* of the corresponding dichlorocyclopropane derivative was detected, although this cyclopropane was observed in a competitive experiment in which dichlorocarbene was generated in the usual way[6,7] in the presence of *both* triphenylphosphine and tetramethylethylene.

The mechanism shown is consistent with the experimental observations:



Acknowledgment.—We wish to thank Dr. Richard W. Young of this Laboratory for his encouragement and helpful discussions.

[6] W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[7] An authentic sample of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane was supplied by Dr. W. A. Henderson, Jr., of this Laboratory, W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **80**, 5274 (1958).

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RECEIVED JANUARY 16, 1962

ON d HYBRIDIZATION IN CHLORINE

Sir:

In a recent communication[1] Klemperer has argued "that the differences in chemical bonding of chlorine and fluorine cannot be naturally explained simply in terms of 3d hybridization." He cites the previously reported spectroscopic energies required to excite a p electron to the 3d level in these two atoms and then bases his argument on "the similarity in magnitude of 3d excitation in chlorine and fluorine" and on their "in each instance being slightly less than two e.v. below the ionization limit."

We question the argument that optical excitation energies for one electron in one center orbitals can be used directly to determine the stability of two electrons in two center orbitals. The argument applied to this particular case seems inappropriate for the following reasons:

(1) Excitation energies of the 3d electrons of *all* elements in the first two rows lie within two e.v. of their ionization energies.[2] For example, if one compares the second row element, sulfur, for which d orbital utilization in certain types of bonding is generally accepted, and the first row group member, oxygen, it is seen that these 3d excitation energies are 1.8 e.v. and 1.5 e.v., respectively, below the ionization energies. Further, there is even closer similarity in the magnitudes of these excitation energies between sulfur and oxygen, than between chlorine and fluorine.[3]

(2) Actually, comparing second to first row elements in the same group, the difference in this p to 3d excitation energy reaches a maximum, 4.7 e.v., for the pair chlorine to fluorine. In fact, it would seem that this particular difference, 108 kcal./mole, is significant because it is greater than the energy released in the formation of most covalent bonds.

(3) It is important to specify the type of bonding considered in discussing this subject. In general, there are two rather distinct ways in which d orbitals are utilized in covalent bonding: one, in added hybridization of atomic orbitals which are largely s and p in character and accommodate an octet of valence electrons (four bonds and/or unshared pairs); to our knowledge, no authors ascribe more than a few per cent. d character in this type of hybridization.[4] Two, given an octet of electrons which exhaust the s and p valence orbitals, it is apparent that second row non-metals can accept additional bonding electrons, either in forming new sigma bonds[5] or in stabilizing adjacent unshared pairs (pi bonding).[6] For this second type of utilization of an atomic orbital, it would seem that rather than optical excitation energy, it is the radius and angular concentration which is

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[1] W. Klemperer, *J. Am. Chem. Soc.*, **83**, 3910 (1961).

[2] C. E. Moore, "Atomic Energy Levels," Vol. I, United States Department of Commerce, 1949, Washington, D. C.

[3] Optical excitation energy related to the s to p promotion, which is the most common in first and second row atomic hybridization, can be readily estimated from Slater's one electron energy table (*Phys. Rev.*, **98**, 1039 (1955)), where it is seen that s to p excitation (even with the same principal quantum number) can require energy in excess of that required for ionization. For example, 2s to 2p for oxygen requires 16.5 e.v., while oxygen's ionization energy is only 13.6 e.v. Yet one would hardly argue on this basis that it is "arbitrary" or not "natural" to assign s character to the sigma bonding orbitals of oxygen.

[4] Some have even found it useful (*cf.*, L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 126 ff.) to consider use of atomic orbitals of energy greater than d (f and g), even those of the energy continuum, in arriving at the hybridization of a bonding orbital.

[5] *Cf.* the numerous polyhalides of the second row non-metals; *e.g.*, ClF_3 and SF_6.

[6] One of the most interesting differences involving chlorine and fluorine, which can be naturally explained with d orbital resonance for the former, is the relatively greater stability of the $X_3C:^-$ ion when X is chlorine than when it is fluorine; for a leading reference see L. H. Slaugh and E. Bergmann, *J. Org. Chem.*, **26**, 3158 (1961). For a discussion of the nature of d orbital hybridization and multiple bond character in the halogen molecules themselves, see R. S. Mulliken, *J. Am. Chem. Soc.*, **77**, 884 (1955).

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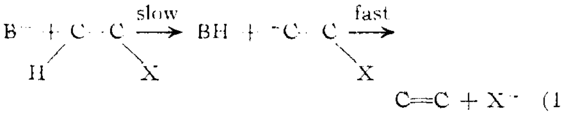
CONCERTED BIMOLECULAR ELIMINATIONS AND SOME COMMENTS ON THE EFFECT OF DIHEDRAL ANGLE ON E2 REACTIONS

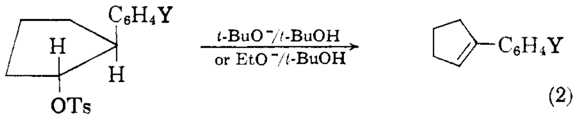
Sir:

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)

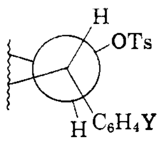
RATE CONSTANTS FOR THE REACTION OF I WITH POTASSIUM t-BUTOXIDE IN t-BUTYL ALCOHOL AT 46.8°

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

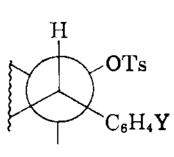
These data fit a Hammett[3,4] plot extremely well, giving $\rho = 2.34 \pm 0.03$. *Under the same conditions a series of β-arylethyl tosylates had* $\rho = 3.39 \pm 0.29$.[5] Clearly this *cis* elimination involves an even smaller amount of carbanionic character on the benzyl carbon, and the elimination 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.