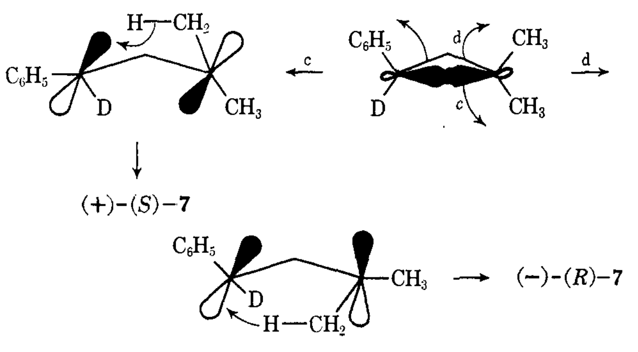
knowledge of the absolute stereochemistry of **6**[12,13] and **7**[14] shows that the reaction takes place with *retention* of *stereochemistry* at the benzylic carbon.

It is worthwhile to carry out a mechanistic evaluation which reflects the minimum retention of stereochemistry value allowed by the error in our data on the optical purity of **7**.[15] Using the extremes of the values for experiment 1 given in Table I for **6** (av) and **7** (obsd) (*i.e.*, 0.64 and 0.30, respectively), it can be calculated that $k_1 = 2.8k_2$, *i.e.*, at a *minimum* retention is faster

$$(+)\text{-}(S)\text{-}\mathbf{7} \xleftarrow[\text{retention}]{k_1} (+)\text{-}(S)\text{-}\mathbf{6} \xrightarrow[\text{inversion}]{k_2} (-)\text{-}(R)\text{-}\mathbf{7}$$

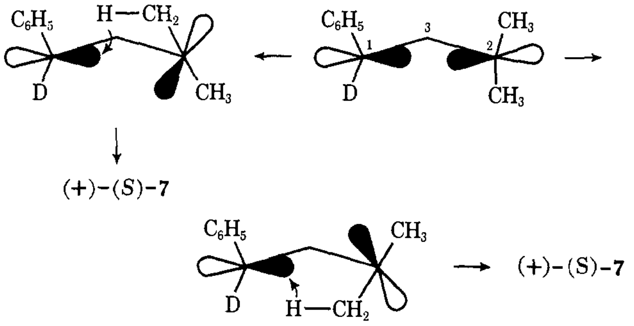
than inversion at the benzylic carbon by a factor of 2.8. In addition to symmetrical intermediates such as **2**,[16] these data also exclude a process where hydrogen migration occurs on ring opening en route to **2**. A pair of disrotatory and conrotatory processes (d and c in Scheme I, respectively) must occur with preferential migration from methyl group trans to the benzene ring. The necessary 63:37[3] trans:cis ratio would result in net *inversion* of stereochemistry, *i.e.*, $k_1/k_2 = 0.6$. A related situation where conrotatory opening (c) results in retention whereas disrotatory opening (d) results in racemization predicts a k_1/k_2 ratio of 2.2, a value excluded by our experimental results.[17]

Scheme I



Although any mechanism or combination of mechanistic pathways which would result in 47% retention of stereochemistry at C1 and 53% racemization will fit the extremes of our experimental data, we consider the following as the most reasonable possibilities. Our data suggest that the probable mechanisms for this reaction be limited to two: a ${}_{\sigma}2_{s} + {}_{\sigma}2_{s}$ concerted cycloaddition reaction subject to a slight steric effect (and thus the preference for trans migration); a reaction which proceeds through a "diradical" formed essentially by expansion of the C_1–C_3–C_2 bond angle (Scheme II).

Scheme II



In this process rotation around the C_1–C_3 bond must be much *slower* than rotation around the C_3–C_2 bond, a proposal consistent with the relative masses of the rotating groups.[18] The net effect is a cleavage of the C_1–C_2 bond followed by a rocking motion at C_2, subject to a slight steric effect, followed by hydrogen migration.

Both of these mechanisms fit the experimental data (*i.e.*, migration from cis and trans methyl groups and generation of optically active product with retention of stereochemistry) and at present we are not able to distinguish between them.

Acknowledgment. We are grateful to the Center of Materials Research of the University of Maryland for partial support of this work.

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[12] The absolute stereochemistry of (+)-**6** is inferred from knowledge of the absolute stereochemistry of (+)-2,2-dimethylphenylcyclopropane[13] and that of its precursor, *E*-2-phenyl-1-methylcyclopropanecarboxylic acid.[9,13] We have assumed that **5** and **6** will have the same sign and magnitude of rotation as their perhydro analogs. Although this assumption is not strictly correct, the error introduced by it is minor.

[13] I. Tomoskozi, *Tetrahedron*, **22**, 179 (1966).

[14] Inferred from its method of synthesis from (*S*)-**8**.[8,9]

[15] Errors were calculated as D. P. Shoemaker and G. W. Garland outlined in "Experiments in Physical Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1967, p 34, and represent our estimates of the 95% confidence limits. The errors in the optical purity of **7** result from low rotations and small sample sizes for **7** and from rather large errors associated with the optical correlation sequence. Data obtained for experiment 1 were clearly superior to those in experiment 2, since more sample was available, and this is reflected in the larger error and fewer significant figures reported in the latter case. Data from experiment 1 were therefore used in the succeeding arguments.

[16] A 90° diradical, where rotation of C1 (fast) has occurred while rotation of C2 has not occurred, also has a plane of symmetry and is ruled out by these results. In this and all other cases we assume that rotation of the phenyl group away from the cyclopropane ring occurs. Examination of models indicates that the alternative rotation, toward the ring, results in severe steric crowding.

[17] In fact the data from experiment 2 are barely within experimental error of this prediction.

[18] Variation of the rates of rotation in trimethylene diradicals has been demonstrated in thermal systems.[19] Stereospecific product formation due to hindered rotation has also been suggested.[20]

[19] R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

[20] J. S. Swenton and A. Wexler, *ibid.*, 93, 3066 (1971).

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A MINDO/3 Study of the Factors Controlling Configurational Stability in Vinyl and Cyclopropyl Radicals[1]

Sir:

The bent geometry of the vinyl radical **1a**[2] and the nonplanar geometry of the cyclopropyl radical **2a**[3] are now well recognized. Recent reports[4,5] indicate that the barriers to inversion are greater in 1-chloro- **(1b)**

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[1] This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and the Robert A. Welch Foundation through Grant F-126.

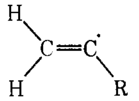
[2] P. H. Kasai, *J. Amer. Chem. Soc.*, **94**, 5950 (1972), and references cited therein.

[3] See M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **91**, 3652 (1969); J. Jacobus and D. Pensak, *Chem. Commun.*, 400 (1969).

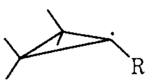
[4] (a) For a review see L. A. Singer in "Selective Organic Transformations," Vol. II, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1972, p 239; (b) M. S. Liu, S. Soloway, D. K. Wedegaertner, and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **93**, 3809 (1971).

[5] (a) T. Ando, H. Yamanaka, F. Namigata, and W. Funasaka, *J. Org. Chem.*, **35**, 33 (1970); (b) L. J. Altman and R. C. Baldwin, *Tetrahedron Lett.*, 2531 (1971). *Cf.*, however, L. A. Singer and J. Chen, *ibid.*, 939 (1971).

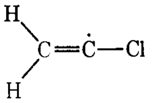
and 1-methoxyvinyl (**1c**) than in **1a** and greater in 1-chloro- (**2b**) and 1-fluorocyclopropyl (**2c**) than in **2a**.



1a, R = H
b, R = Cl
c, R = OCH$_3$



2a, R = H
b, R = Cl
c, R = F



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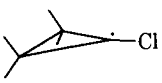

4

As Walsh[6] pointed out some time ago, the 2p character of the AO used by carbon to form a CX σ bond in CY$_3$X should be greater the more electronegative X is. The bond angles YCX should therefore decrease as the electronegativity of X increases. Walsh cited a number of examples in support of this idea and Pauling[7] and others[8] have recently used it extensively to interpret molecular geometries. If the CR bonds in **1** and **2** are essentially single, one would then expect an increase in the electronegativity of R to lead to a decrease in the equilibrium CCR angle and to a corresponding increase in the barrier to inversion.

On the other hand much evidence suggests that radicals such as **1b** or **2b** are stabilized by the formation of three-electron π bonds from the substituent to the radical center.[9] Since such π bonding should be more effective in **1** when the trivalent carbon is linear and in **2** when it is planar, one might have expected the barrier to inversion to be less in **1b** or **1c** than in **1a** and less in **2b** or **2c** than in **2a**.

In view of this apparent contradiction, we have examined **1** and **2** and the transition states for their inversion, using the latest version of the MINDO method (MINDO/3)[10] in conjunction with energy partitioning.[11,12]

The two-center electronic energies, which are measures of bond strengths,[11] calculated for **1b**, the transition state **3** for inversion of **1b**, **2b**, and the transition state **4** for inversion of **2b**[13] reveal that the CCl bond strengths fall in the order **1b** ≫ **3** and **2b** ≫ **4**. The enhanced barrier to inversion of both **1b** and **2b** is therefore due to a large antibonding interaction between the chlorine and the radical center in **3** and **4** which is not present in **1b** and **2b**. Examination of the MO's in **3** and **4** shows that the antibonding effect arises from a σ–π interaction involving the "singly occupied" carbon 2p AO, a 3p AO of chlorine, and the CH bonds of the adjacent methylene group(s). This situation can be interpreted by the following extension of the PMO method.[9]

In the chloromethyl radical (ClCH$_2$·) a π interaction (Figure 1a) between a filled chlorine 3p AO and the singly occupied carbon AO lowers the energy of the former and raises the energy of the latter. In the simple PMO approach,[9] both changes are assumed to be equal so that the net effect is a large stabilization. Since, however, antibonding MO's are in fact more antibonding than corresponding bonding ones are bonding,[9] the increase in energy of the singly occupied MO is greater than the decrease in that of the filled one. The overall effect is still bonding but relatively small.

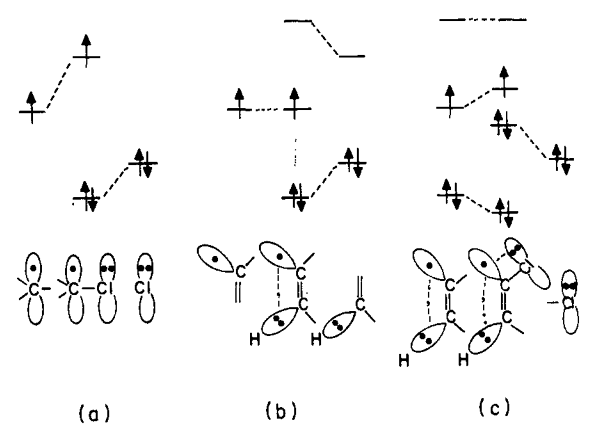

Figure 1. (a) Interaction of AO's of C and Cl in ClCH$_2$·. (b) Interaction of CH MO's with singly occupied C AO in **1a**. (c) Interaction of 3p AO of Cl with allyl-type[9] MO's of vinyl in **1b**.

In **1a** a hyperconjugative interaction (Figure 1b) between the CH bond MO's[14] and the singly occupied carbon AO leads to a set of three allyl-type[9] three-center MO's, one bonding, one nonbonding, and one antibonding. In **1b** the 3p AO of chlorine interacts with these three MO's (Figure 1c).

The interaction between the chlorine AO and the singly occupied nonbinding MO will be weakly bonding (*cf.* Figure 1a). The interaction between chlorine and the filled MO will, however, be strongly antibonding because it involves an interaction between two filled orbitals. The net result will depend on the relative magnitudes of these two conflicting effects.[15]

The interaction between two orbitals is greater, the better they overlap in space. The magnitudes of the interactions between chlorine and the two three-center MO's will then depend on the orbital densities in the latter at the carbon atom adjacent to chlorine. These in turn will depend on the extent of the coupling between the CH orbitals and the singly occupied carbon AO. If this is small, the two bonding electrons will remain almost localized in the CH region while the unpaired electron will be concentrated on the carbon atom adjacent to chlorine. Under these conditions the net interaction with chlorine will be bonding because only the singly occupied MO will interact effectively with chlorine. As the CH–C coupling increases, the three electrons involved will become increasingly delocalized. The density of the occupied MO at the carbon atom adjacent to chlorine will then increase while that of the singly occupied MO will correspondingly decrease. The net interaction with chlorine will consequently become progressively more antibonding.

The CH–C coupling will naturally be less in bent **1**

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(6) A. D. Walsh, *Discuss. Faraday Soc.*, **2**, 21 (1947).

(7) L. Pauling, *J. Chem. Phys.*, **51**, 2767 (1969).

(8) See, *e.g.*, A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc. A*, 124 (1971).

(9) See M. J. S. Dewar, "Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(10) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, to be submitted for publication. See also N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5303 (1972), and earlier papers in this series.

(11) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **16**, 163 (1970).

(12) M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **93**, 7201 (1971).

(13) The geometries were optimized by the Simplex method: A. Brown, M. J. S. Dewar, H. Metiu, P. J. Student, and J. Wasson, to be submitted for publication.

(14) In Figure 1 we have for simplicity written a single CH bond as the interacting species. As in other cases of hyperconjugation, the methylene group will behave in this way, *i.e.* like the group C=X.

(15) Note that the other CCl interactions, between the other chlorine lone pair and the π MO's of the C=C bond, are independent of the CCCl bond angle and can consequently be disregarded in the present connection.

than in linear **1** and less in nonplanar **2** than in planar **2**. The antibonding effect of chlorine must consequently be greater in **3** than in **1b** and greater in **4** than in **2b**. This of course at once explains the enhancement of the barrier to inversion by chlorine.

The CH–C interaction should also be greater, the shorter the CC bond. One would therefore expect the effect of chlorine in stabilizing unsymmetrical conformations to decrease in the order vinyl ≫ cyclopropyl > alkyl, the CC bond lengths in the corresponding hydrocarbons being 1.34, 1.51, and 1.53 Å, respectively.[10] This appears to be the case.[4,5]

The calculations reported here thus suggest that the enhanced barriers to inversion in **1b**, **1c**, **2b**, and **2c** may be due primarily to a novel type of π destabilization rather than to the Walsh electronegativity effect. In any case the apparent contradiction noted earlier is removed since both effects act in the same direction.

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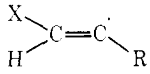
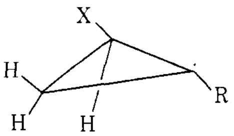
Antagonism between Substituents in Radicals[1]

Sir:

The configurational stabilities of vinyl and cyclopropyl radicals having substituents at the radical center (*e.g.*, **1a,b** and **2a,b**) are greater than those of the unsubstituted species (**1c** and **2c**).[2] We have shown[3] that this is probably due to a novel type of antibonding interaction between lone-pair electrons of the substituent and the MO's arising from interactions between the singly occupied carbon AO and the MO's of adjacent C–H bonds. Since this implies the existence of a new and unsuspected substituent effect of obvious importance in radical chemistry, we have investigated it further.



1a, R = Cl; X = H
b, R = OCH_3; X = H
c, R = H; X = H
d, R = Cl; X = Cl
e, R = Cl; X = CH_3
f, R = Cl; X = C_6H_5
g, R = OCH_3; X = CH_3



2a, R = Cl; X = H
b, R = F; X = H
c, R = H; X = H
d, R = Cl; X = Cl
e, R = Cl; X = CH_3

Consider a radical $\cdot CHAB$ where A and B are substituents either with lone pairs (*e.g.*, Cl, OM) or σ bonds (*e.g.*, CH_3) that can interact with the singly occupied carbon AO. We can construct $\cdot CHAB$ in steps by the successive union of $\cdot CH_3$ with A and B. First, consider union with A (Figure 1a). Interaction between the filled orbital with A and the singly occupied one of $\cdot CH_3$ results in a filled bonding MO and a singly occupied antibonding one. Since the splitting is not symmetrical, the increase in energy of the singly occupied orbital being greater than the decrease of the doubly occupied one, the net effect is only weakly bonding. The resulting mesomeric stabilization of the radical will be greater, the nearer together the orbitals are in energy and the greater the A–C resonance integrals.

Next consider union of $\cdot CH_2A$ with B (Figure 1b). The interaction between the two filled orbitals will be antibonding while that between the filled orbital of B and the singly occupied one of $\cdot CH_2A$ will be weakly bonding. Since the singly occupied orbital is higher in energy than the AO of methyl (Figure 1a), the net stabilizing effect of B is less than it would be on methyl itself (Figure 1c). Indeed, the net effect of B may even be destabilizing since the antibonding interaction between the filled orbitals of $\cdot CH_2A$ and B may outweigh the bonding one. The substituents do not therefore act in unison; rather, they antagonize one another.

The net antibonding interaction will be greater, the greater the density of the doubly occupied MO of $\cdot CH_2A$ at carbon and the less that of the singly occupied one. It will also be greater, the closer together the doubly occupied orbitals of $\cdot CH_2A$ and B and the larger the B–C resonance integral. The relevant orbital densities will be greater, the stronger the interaction between the doubly occupied orbital of A and the singly occupied orbital of carbon in $\cdot CH_2A$. This in turn will be greater, the higher the energy of the orbital of A and the greater the C–A resonance integral. The antagonism will therefore increase: (a) with an increase in the C–A resonance integral; (b) with an increase in the C–B resonance integral; (c) with an increase in the energy of the orbital of A; (d) the closer together are the orbitals of A and B in energy. The effect should therefore be greatest when A and B are the same, when the relevant orbitals on them are AO's (since the corresponding resonance integral to carbon is then greater), and the higher the energies of the AO's.

The C–A and C–B resonance integrals will be greatest when the carbon AO is a 2p AO, *i.e.* for planar methyl radicals and linear vinyl ones. The resulting increase in antagonism will therefore favor a pyramidal structure for the former and a bent structure for the latter. The barrier to inversion should be greater, the greater the overall antagonism between A and B, *i.e.*, the higher the energy of the orbital of A and the closer together the energies of the orbitals of A and B.

The available evidence supports these conclusions. Thus while methyl radical is planar,[4] trifluoromethyl,[5] trichloromethyl,[6] and *tert*-butyl[7] are pyramidal.[8,9] Walsh[11] some time ago pointed out that the hybridiza-

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[1] This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and the Robert A. Welch Foundation through Grant F-126.

[2] (a) L. A. Singer in "Selective Organic Transformations," Vol. II, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1972, p 239; (b) M. S. Liu, S. Soloway, D. K. Wedegaertner, and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **93**, 3809 (1971); (c) T. Ando, H. Yamanaka, F. Namigata, and W. Funasaka, *J. Org. Chem.*, **35**, 33 (1970); (d) L. J. Altman and R. C. Baldwin, *Tetrahedron Lett.*, 2531 (1971); (e) L. A. Singer and J. Chen, *ibid.*, 939 (1971).

[3] R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **95**, 7180 (1973).

[4] G. Herzberg, "The Spectra and Structures of Single Free Radicals," Cornell University Press, Ithaca, N. Y., 1971.

[5] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 43, 2704 (1965); D. E. Milligan and M. E. Jacox, *ibid.*, **48**, 2265 (1968).

[6] L. Andrews, *J. Chem. Phys.*, **48**, 972 (1968); T. L. Leggett and D. A. Kohl, *J. Chem. Phys.*, submitted for publication. We are grateful to Dr. D. A. Kohl for telling us his unpublished results.

[7] D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Latham, *J. Amer. Chem. Soc.*, **94**, 6241 (1972).

[8] For Additional examples see A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc. A*, 124 (1971).

[9] Recently doubt has been expressed[10] concerning the nonplanarity of *tert*-butyl. See, however, ref 8.

[10] M. C. R. Symmons, *Tetrahedron Lett.*, 207 (1973).

[11] A. D. Walsh, *Discuss. Faraday Soc.*, **2**, 21 (1947).