suggested by Bigeleisen.[15] Those results are explained if there are presumed to operate one or more rapid reversible equilibria prior to the rate-determining step in the decarboxylation which affect the binding about the carboxyl carbon atom(s). The data in Table II indicate that the decarboxylation of the diacid in the presence of quinoline is a bimolecular process. While the isotope effect results do not permit one to reach a definite conclusion concerning the natures of the solvation equilibria, calculation[2] shows that proton transfer cannot be the rate-determining process; such a conclusion seems to reduce the likelihood that activation proceeds by proton shift from a solvation equilibrium such as hydrogen bonding of the carboxyl groups with solvent (quinoline) molecules.

4. Examination of models shows that steric hindrance of various amines might interfere with their catalytic ability. The relative rates of malonic acid decarboxylation in the presence of the six amines listed in Table I (runs V-13 to 16) are commensurate with the expected hindrance.

Of course, the direct evidence for the participation of the amine in the decarboxylation of the free acid consists of the dependence on the amine concentration of the rate of reaction, and the large negative entropy of activation. The latter is much more negative than the value which would be expected if formation of the activated complex involved minor rearrangements of solvent molecules (*i.e.*, rearrangements which are incident to activation but not so extreme as to result in solvent concentration dependence of the reaction rate). Comparison of the thermodynamic data in Table II indicates clearly that in water and quinoline media the reaction mechanisms are very different for free acid decarboxylation, while they may be similar for that of the monoanion.

Hall[5] has shown that acid catalysis is not important in aqueous solution decarboxylation, and our data for decomposition in dioxane indicate that the dielectric constant of the medium is not an important factor in the case of the free acid as it is for the monoanion. It is therefore probable that the decarboxylation of un-ionized malonic acid is a simple thermal reaction in the absence of amine catalysts.[3,4,16,17]

Acknowledgments.—This research was supported by the A.E.C. We are grateful for the interest and helpful suggestions of Dr. E. J. Corey. We are indebted to Miss Helen Miklas for the infrared determinations.

---

[15] J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

[16] B. R. Brown, *Quarterly Rev.*, **5**, 131 (1951).

[17] R. A. Fairclough, *J. Chem. Soc.*, 1186 (1938).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE INSTITUTO DI CHIMICA GENERALE E ANALITICA OF THE POLITECNICO DI MILANO, ITALY, GATES AND CRELLIN LABORATORIES, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Neighboring Carbon and Hydrogen. XVI. 1,3-Interactions and Homoallylic Resonance

BY M. SIMONETTA[1] AND S. WINSTEIN[2]

RECEIVED MARCH 16, 1953

Evidence from stereochemistry and reaction kinetics suggests the existence of an important 1,3-interaction between a carbonium ion center and a π-electron-containing β-substituent. A semi-empirical molecular orbital method has been used to estimate the stabilization due to π-electron delocalization in the case of a vinyl, diolefinic or phenyl group beta to a cationic carbon center. Even at the unmodified 1,3 C–C distance of 2.5 Å., a slight stabilization due to electron delocalization is found, the 1,3-overlap integrals, with proper orientation, being appreciable. Considerable compression of the 1,3-distance is more than compensated for by increase in resonance energy; the intervening methylene group is in effect a poor insulator against interaction of the unsaturated centers. The net stabilizations are estimated as *ca.* 10, 6 and 4 kcal./mole for β-dienyl, β-vinyl and β-phenyl, in accord with the rate-enhancing effects of these substituents in solvolysis.

Evidence from stereochemistry and reaction kinetics suggests the existence of an important interaction between a carbonium ion center and a π-electron-containing β-substituent such as a vinyl or phenyl group. This is true for *homoallylic* cases such as cholesteryl I[3] and dehydronorbornyl V[4] and *homobenzyl* cases such as benzylmethylcarbinyl VI.[5,6] Thus cholesteryl derivatives have enhanced rates of ionization,[3] ascribed to delocalization of the electron cloud of the neighboring olefinic group in the rate-determining step.[3] This participation of the 5,6-olefinic group in the substitution process gives rise to a non-classical ion[3,5] which has been written as II (canonical structures IIa and IIb) with partial 3,5-bonding and weakened 5,6-bonding. This intermediate reacts[3] with nucleophilic species at C$_6$ to yield 3,5-cyclosteroids III or at C$_3$ to yield cholesteryl derivatives IV with over-all retention[3,5] of configuration from I to IV.

The concept of the hybrid allyl ion VII is familiar, but the non-classical structure II represents a hybrid structure for the next homologous case, with a methylene group interposed between the cationic center and the π-electron system; this is the reason

---

[1] Arthur A. Noyes Fellow in Chemistry, California Institute of Technology, 1951–1952.

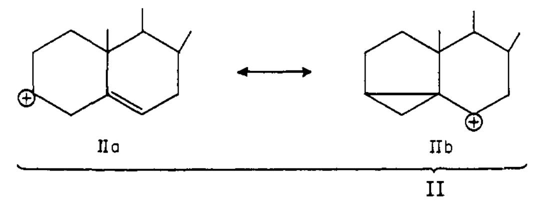
[2] Research supported in part by the Office of Naval Research.

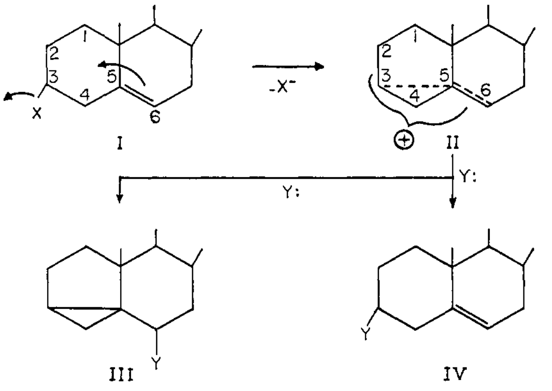
[3] (a) S. Winstein and R. Adams, THIS JOURNAL, **70**, 838 (1948); (b) S. Winstein and A. H. Schlesinger, *ibid.*, **70**, 3528 (1948).

[4] S. Winstein, H. M. Walborsky and K. C. Schreiber, *ibid.*, **72**, 5795 (1950).

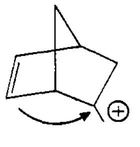
[5] S. Winstein, *Bull. soc. chim.*, **18**, 55C (1951).

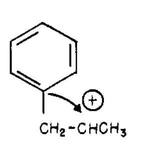
[6] S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, THIS JOURNAL, **74**, 1140 (1952).



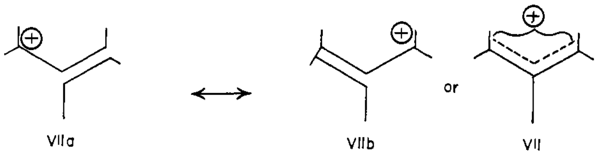


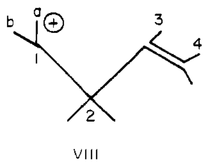
for the *homoallylic designation.* The possible existence of an important 1,3-interaction even in the homoallylic case has interesting implications in organic chemistry. We report in the present paper the results of semi-empirical calculations of the stabilization to be expected from such interaction of a cationic center with an olefinic group, a diolefinic group and a phenyl group.


V

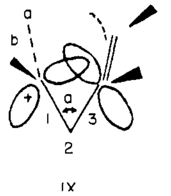


VI





VIII



IX

The 1,3-interaction in the homoallylic ion VIII can be considered[5,7] in a first approximation to involve overlap of the p-orbital on C_3 with what would have been a vacant orbital on C_1, resulting in delocalization of the 3,4-π-electron cloud. With regard to preferred geometry there can be expected a fundamental difference between the allyl and homoallyl cases. The allyl cation is planar, for this is the configuration favorable to π-electron delocalization. On the other hand, a planar arrangement for atoms C_1, C_2, C_3, C_4, a and b is unfavorable in the homoallylic ion because it makes 2pπ-overlap the basis of the 1,3-interaction and π-overlap falls off rapidly with increasing internuclear distance. (For example, the Slater overlap integral[8] for 2pπ-overlap is smaller than for 2pσ-overlap by factors of 3 at a distance of 2.00 Å., 4 at 2.41 Å. and 5 at 2.78 Å.) If the axes of the vacant p-orbital of C_1 and the p-orbital of C_3 are made to lie in the C_1–C_2–C_3 plane as illustrated in IX, considerably improved overlap,[5] intermediate between π and σ, is attained. Our calculations have been made for this orientation with various values of the 1,3-interatomic distance $R_{1,3}$ (the overlap is naturally improved[9] by decrease in $R_{1,3}$), the calculated delocalization or resonance energy, R.E., at each $R_{1,3}$ being corrected for the estimated strain energy, S.E., due to compression of the corresponding C_1–C_2–C_3 angle α, to yield a total energy, T.E. The estimates of both R.E. and S.E. would naturally be affected, and therefore the estimate of the net stabilization, −T.E., due to the 1,3-interaction would be increased, by proper rehybridization of atomic orbitals on atoms C_1, C_2, C_3 and C_4. However, sp^2-hybridization on C_1, C_3 and C_4 and sp^3-hybridization on C_2 have been maintained throughout the present calculations. While the latter are admittedly crude for this and other reasons, the results are nevertheless quite instructive.

The delocalization energies R.E. for the two-electron, three-orbital problem presented by the electrons and orbitals of the double bond and the p-orbital of C_1 were calculated by a semi-empirical molecular orbital (LCAO) method.[10] All Coulomb integrals were assumed equal. Overlap integrals S between the p-orbitals of C_1 and C_3 were numerically evaluated with Kopineck's tables,[11] assuming Z, the effective nuclear charge, to be 3.09 for 2 p-orbitals on C atoms. The exchange integrals β were estimated by using Mulliken's assumption[12] that the energy B of an electron-pair bond is given by equation 1 and the assumption that the exchange integral is a nearly constant fraction of the bond energy. On this basis the β's are related by equation[13] 2, where the prime refers to the 1,3-interac-

$$B = AIS/(1 + S) \tag{1}$$

$$\frac{\beta'}{\beta} = \frac{B'}{B} = \frac{A'I'S'/(1 + S')}{AIS/(1 + S)} \tag{2}$$

tion and its absence to the 3,4-interaction. In equation 2, A' and A and I' and I were cancelled, as is appropriate enough for the valence-state ionization potentials if perhaps not for the constants[12b] A and A' (Mulliken's values being 1.16 for σ-bonds and 1.5 for π-bonds), and S and β were set equal to 0.28 and the usual value −20 kcal./mole, respec-

---

[7] R. Dodson and B. Riegel, *J. Org. Chem.*, **13**, 424 (1948).

[8] R. S. Mulliken, *et al.*, *J. Chem. Phys.*, **17**, 1248 (1949).

[9] S. Winstein, *Bull. soc. chim.*, **18**, 123C (1951).

[10] (a) R. S. Mulliken, *Phys. Rev.*, **41**, 49 (1932); (b) R. S. Mulliken, *J. Chem. Phys.*, **3**, 375 (1935); (c) C. A. Coulson, "Valence" Oxford Press, New York, N. Y., 1952, Chapter IV and further.

[11] H. J. Kopineck, *Z. Naturforsch.*, **5A**, 420 (1950).

[12] (a) R. S. Mulliken, THIS JOURNAL, **72**, 4493 (1950); (b) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

[13] This assumption seems a reasonable one. In a treatment of the butadiene molecule it gives a value for the delocalization energy of 7.6 kcal./mole, superior to the value obtained by the usual molecular orbital LCAO method of 9.6 kcal./mole, and in agreement with the valence-bond value of 7.9 kcal./mole [M. Simonetta, *J. chim. phys.*, **49**, 68 (1952)].

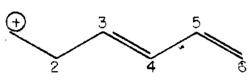
tively. The secular equation was then solved (with omission of the term $-SW$ in the off-diagonal matrix elements) to obtain the energy levels for the three resultant molecular orbitals, and the value $2(Q + \beta)$ for a pair of electrons in a localized 3,4-π-bond was subtracted from twice the lowest energy level to obtain R.E.

We have estimated S.E. by the method of Kilpatrick and Spitzer,[14] which, following Pauling's discussion,[15] assumes that the energy of the angle-strained system is just the sum of energies of the "bent" σ-bonds, each being proportional to the product of the angle-dependent factors, measured along the lines joining the two nuclei, of the bond orbitals involved. In particular, we have used equation 3 where B is the normal C–C bond energy, θ and θ' are the angles by which the axes of

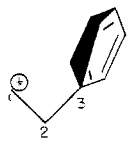
$$\text{S.E.} = 2B[0.996 - (0.5 + 1.5 \cos \theta)(0.577 + \sqrt{2} \cos \theta')/4] \quad (3)$$

the bond orbitals, respectively sp^3 and sp^2, at the two ends of each σ-bond deviate from the internuclear line ($\theta = \theta'$ was assumed[16]) and the two trigonometric factors are the relevant orbital strengths. Since the appropriate value for B is in some doubt[17] for several reasons, the calculation was made for two values, 59 and 66.6 kcal./mole.[18]

Similar calculations were made for the system with two olefinic linkages X and the homobenzyl system XI. The 1,3-integrals and S.E. were treated as before, the 5,6- and intraphenyl-integrals were treated like the 3,4-integral before, and the 3,4- and 4,5-integrals were set equal to 0.89 β.



X



XI

The calculations are summarized in Tables I and II.

Table I

Summary of Calculations for Homoallyl Cation IX

$R_{1,3}$, Å.	S'	β'/β	$-$R.E.^{a}	S.E.^{a} B = 59	S.E.^{a} B = 66.6	T.E.^{a} B = 59	T.E.^{a} B = 66.6
2.51	0.072	0.30	1.8	0.0	0.0	1.8	1.8
2.35	.117	.47	4.2	0.9	1.1	3.3	3.1
2.15	.180	.68	8.3	2.8	3.2	5.5	5.1
1.95	.247	.88	13.2	6.1	7.0	7.1	6.2*
1.75	.302	1.03	17.4	10.2	11.6	7.2*	5.8
1.63	.322	1.08	18.8	12.9	14.7	5.9	4.1
1.54	.332	1.11	19.7	14.7	16.8	5.0	2.9

^{a} R.E., S.E. and T.E. values are in kcal./mole.

Table II

Summary of Calculations for X and XI

$R_{1,3}$, Å.	X $-$R.E.^{a}	X T.E.^{a} B = 59	X T.E.^{a} B = 66.6	XI $-$R.E.^{a}	XI T.E.^{a} B = 59	XI T.E.^{a} B = 66.6
2.51	2.0	2.0	2.0	1.2	1.2	1.2
2.35	5.2	4.3	4.1	3.6	2.7	2.5
2.15	10.4	7.6	7.2	6.8	4.0	3.6
1.95	16.4	10.3	9.4	11.2	5.1*	4.2*
1.75	21.2	11.0*	9.6*	15.2	5.0	3.6
1.63	22.8	9.9	8.1	16.4	3.5	1.7
1.54	24.0	9.3	7.2	17.2	2.5	0.4

^{a} In kcal./mole.

The calculated values of S' and R.E. show that the 1,3-overlap is great enough to be of some chemical importance[9] even at the normal distance 2.5 Å., and for smaller values of $R_{1,3}$ (and α) the net stabilization rises to quite sizable maxima, indicated by asterisks in Tables I and II, where the forces of angle strain and C_1–C_3 stretching balance.

The present calculations are instructive in stressing how little insulation against interaction between unsaturated centers may be provided by an intervening methylene group[19] if the assumed orientation is accessible. Indeed, the $-$T.E. of *ca.* 6 kcal./mole for the homoallylic ion is 40% as great as the corresponding delocalization energy $[(2\sqrt{2} - 2)\beta = 16.4$ kcal./mole$]$ of the allyl cation. 1,3-Interactions may well give rise to other effects such as the interaction between non-adjacent chromophores[20,21] observed for 9,10-dihydroanthracene, triptycene,[20] 2,5-dihydroacetophenone,[21] etc., as pointed out by Bartlett and Lewis.[20] There has been a certain tendency,[21] however, to reject direct 1,3-interactions in the excited state in light absorption and to stress hyperconjugation.

As might have been expected, the order of stabilization dienyl > vinyl > phenyl found for these groups in the β-position is the same as the order found previously for ordinary (α) conjugation of these groups with an olefinic linkage (ref. 10c, p. 235; ref. 15, p. 202). Furthermore, it is the order of the rate-enhancing effects of the β-substituents in solvolysis.[3–6,22] For example, the rates of solvolysis of cholestanyl XII, cholesteryl XIII and 7-dehydrocholesteryl[23] XIV p-toluenesulfonates are in the ratio 1:100:3000. These figures correspond to stabilization of the transition states for XIII and XIV by *ca.* 3 and 5 kcal./mole even though the orientation of the β-substituent is not the ideal one.

---

(14) J. E. Kilpatrick and R. Spitzer, *J. Chem. Phys.*, **14**, 463 (1946). See J. D. Dunitz and V. Schomaker, *ibid.*, **20**, 1703 (1952).

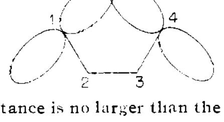
(15) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, chapter III.

(16) This assumption was of course also made in the calculation of S' and β'.

(17) See for example, L. Pauling and W. F. Sheehan, *Proc. Nat. Acad. Sci.*, **35**, 359 (1949).

(18) Other modifications were explored. In one calculation, for example, θ' was varied so as to maximize $S_{1,2}$; equation 3 was evaluated with $B = 80$ kcal./mole; and $I = I'$ and $A = 1.5$ were assumed in equation 2, while A' was varied to suit the σ-character of the 1,3-bond. The resulting $-$T.E. values go through a maximum of 8.90 kcal./mole at $R_{1,3} = 1.75$ Å.

(19) Although no calculations are presented here for 1,4-interactions across two methylene groups, it is clear that the configuration favors relatively strong interaction, as was first pointed out to us by L. deVries. The 1,4-distance is no larger than the original $R_{1,3}$ in IX, X, and XI, and the relative orientation of orbitals on C_1 and C_4 is more conducive to effective overlap. Considerations of this sort are pertinent to valency tautomerism questions.

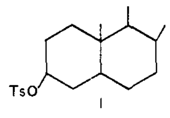


(20) *E.g.*, P. D. Bartlett and E. S. Lewis, This Journal, **72**, 1005 (1950).

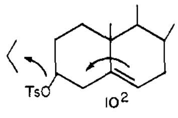
(21) *E.g.*, E. A. Braude, *et al.*, *J. Chem. Soc.*, 607, 1902 (1949).

(22) S. Winstein, *et al.*, This Journal, **74**, 1113 (1952).

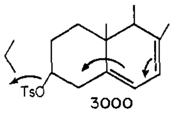
(23) N. J. Holness, unpublished work.



XII

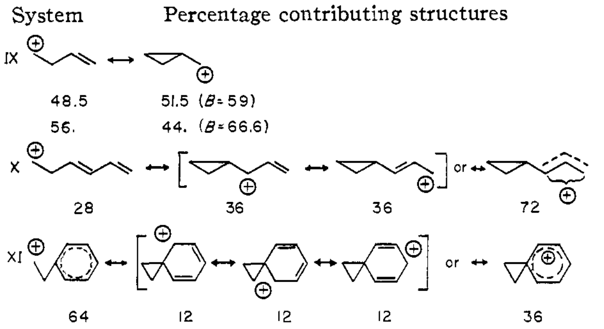


XIII

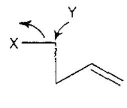


XIV

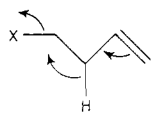
The electron distributions for the most stable configurations of IX, X and XI were obtained by calculating the coefficients of the atomic orbitals in the bonding molecular orbital. The following resonance descriptions correspond to the same net atomic charges:



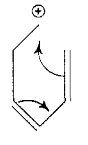
The possibility of substantial stabilization *via* 1,3-interaction does not, of course, guarantee that reaction will proceed only in the indicated way; other, competing paths of reaction must, as usual, be considered. These may involve displacement by solvent or another nucleophilic reagent (XV), hydrogen participation (XVI), assisted[5,22] by a β-vinyl or similar group, or other kinds of cyclization, *e.g.*, XVII. Thus the simplest homoallyl alcohol, allylcarbinol, reacts without rearrangement[24]



XV



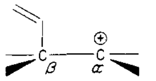
XVI



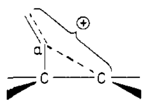
XVII

with reagents such as thionyl chloride or phosphorus tribromide. Benzylmethylcarbinyl *p*-toluenesulfonate solvolyzes predominantly without phenyl participation in ethanol and acetic acid, but predominantly with phenyl participation in formic acid.[6] When allylcarbinylamine is diazotized, hydrogen shift, with formation of crotyl and α-methylallyl alcohols is a competing process.[24] Similarly, hydrogen shift is more or less important in solvolysis of epicholesteryl[25] and 3-phenyl-2-butyl[26] derivatives. With (γ,γ-dimethylallyl)-carbinyl,[27] cholesteryl[3,7,25] and dehydronorbornyl[28] derivatives, other competing processes are apparently much more nearly completely excluded.

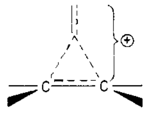
Moreover, the present calculations do not preclude further delocalization leading to different or additional structures. Thus, homoallyl and homobenzyl effects can merge[5,6] with the Wagner–Meerwein rearrangement. Additional delocalization involving the bonding electrons "a" in XIX, (formed from XVIII) can lead to the symmetrical ion XX. Similarly, further electron delocalization in a homobenzyl ion can lead to a phenyl-bridged structure.[6,29] As pointed out previously,[5,6] in neither the homoallyl nor homobenzyl cases is it entirely clear how many cationic species require explicit mention in any specific case. In the dehydronorbornyl,[28,30,31] β-phenylethyl[30b,32] and 4-phenyl-3-hexyl[33] cases, there has been some discussion of possible evidence for both symmetrical (*e.g.*, XX) and unsymmetrical (*e.g.*, XIX) non-classical cations.[34]



XVIII



XIX



XX

---

[24] J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951).

[25] E. Kosower, Ph.D. Thesis, U.C.L.A., 1952; D. D. Evans and C. W. Shoppee, *J. Chem. Soc.*, 540 (1953).

[26] D. J. Cram, THIS JOURNAL, **74**, 2137 (1952).

[27] (a) P. Bruylants and A. Dewael, *Bull. classe. sci. acad. roy, Belg.*, [5] **14**, 140 (1928); (b) T. A. Favorskaya and S. A. Fridman. *J. Gen. Chem.* (*U.S.S.R.*), **15**, 421 (1945).

[28] H. J. Schmid, unpublished work.

[29] D. J. Cram, THIS JOURNAL, **71**, 3863 (1949).

[30] J. D. Roberts, (a) Organic Reaction Mechanisms Symposium, New York, Sept., 1951; (b) Organic Reaction Mechanisms Conference, Bryn Mawr, Pa., Sept., 1952.

[31] S. Winstein, Organic Reaction Mechanisms Conference, Bryn Mawr, Pa., Sept., 1952.

[32] J. D. Roberts and C. M. Regan, THIS JOURNAL, **75**, 2069 (1953).

[33] D. J. Cram, Organic Reaction Mechanisms Conference, Bryn Mawr, Pa., Sept., 1952; D. J. Cram and F. A. Abd Elhafez, THIS JOURNAL, **75**, 3189 (1953).

[34] With the simplest homoallyl derivatives there is a further complication, since, for example, allylcarbinylamine gives rise to cyclobutanol as well as cyclopropylcarbinol.[24] The number of cationic species involved and their formulation are not yet clear[30a] [J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 3542 (1951); M. J. S. Dewar, *Ann. Repts.*, **48**, 120 (1951)].