Table II. Results Obtained upon the Addition of Pr(dpm)$_3$ or Ni(acac)$_2$

1

2

3

4

5

6

7

8, R = H
9, R = OH

10, R = H
11, R = NO$_2$
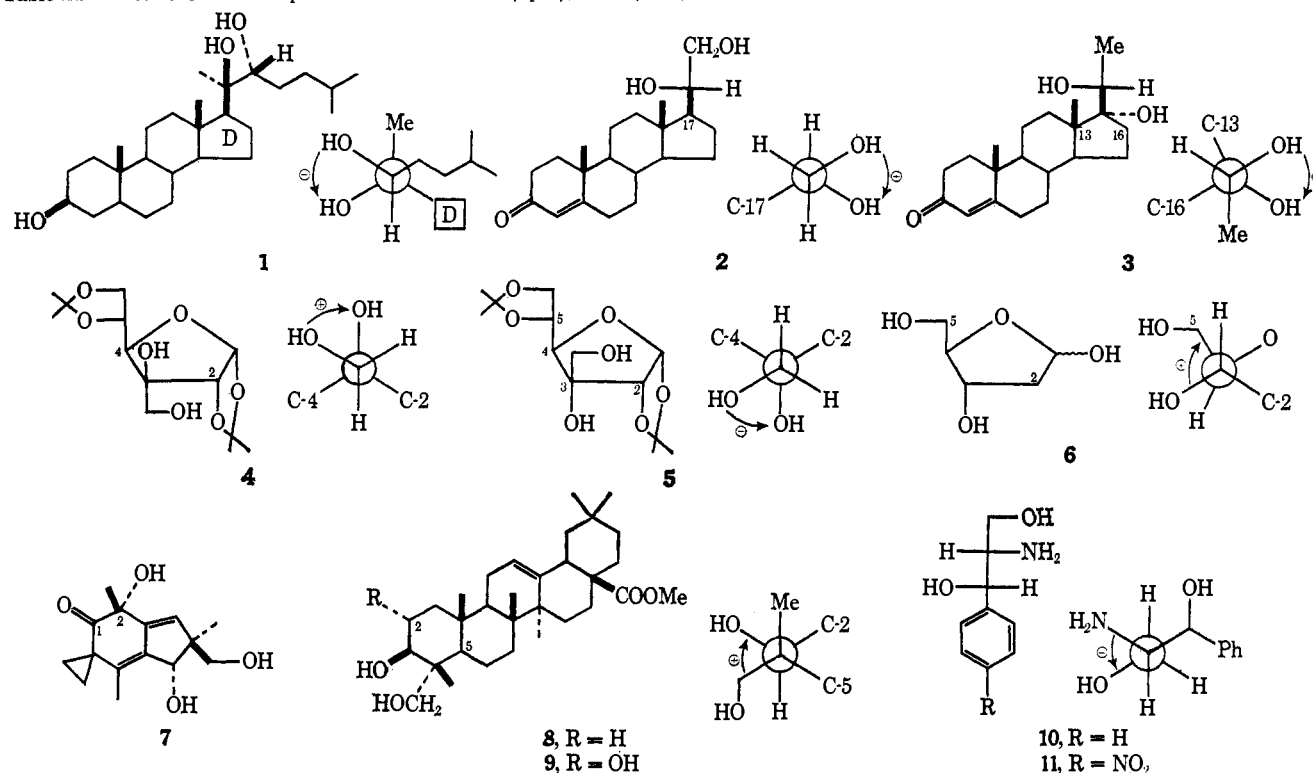
Entry	Reagent	Concentration (reagent) (M)	Molar ratio (sub/reag)	CD^a	Method
1	Pr(dpm)$_3$	1.0×10^{-4}	b	$\Delta\epsilon_{303} = -8.2$	Hexane
2	Ni(acac)$_2$^{d}	5.0×10^{-5}	2/1	$\Delta\epsilon_{311} = -0.6^c$	0.2 M t-BuOH–CCl$_4$ at 10°
		1.0×10^{-3}	2/1	$\Delta\epsilon_{640} = +0.003$	CCl$_4$
3	Ni(acac)$_2$	2.5×10^{-5}	3/1	$\Delta\epsilon_{319} = -3.0$	0.2 M t-BuOH–CCl$_4$
4	Ni(acac)$_2$^{f}	5.6×10^{-5}	200/1	$\Delta\epsilon_{316} = -1.0$	50% t-BuOH–CCl$_4$
5	Ni(acac)$_2$^{f}	5.6×10^{-5}	200/1	$\Delta\epsilon_{315} = +0.9$	50% t-BuOH–CCl$_4$
6	Ni(acac)$_2$	4.9×10^{-5}	200/1	$\Delta\epsilon_{315} = -0.7$	50% t-BuOH–CCl$_4$
7	Ni(acac)$_2$^{d}	5.0×10^{-5}	2/1	$\Delta\epsilon_{315} = +3.3$	0.2 M t-BuOH–CCl$_4$ at 10°
8	Ni(acac)$_2$^{g}	5.0×10^{-5}	2/1	$\Delta\epsilon_{315} = -1.0$	0.2 M t-BuOH–CCl$_4$
9	Pr(dpm)$_3$	1.04×10^{-4}	6/1	$\Delta\epsilon_{313} = +1.5$	CCl$_4$
	Ni(acac)$_2$	1.0×10^{-3}	9/1	$\Delta\epsilon_{314} = -23.6$	CCl$_4$
		1.0×10^{-3}	9/1	$\Delta\epsilon_{635} = +0.02$	CCl$_4$
10	Ni(acac)$_2$	4.7×10^{-5}	15/1	$\Delta\epsilon_{315} = +7.1$	0.2 M t-BuOH–CCl$_4$
11	Ni(acac)$_2$	6.0×10^{-5}	10/1	$\Delta\epsilon_{315} = +7.0^e$	2% t-BuOH–CCl$_4$

^{a} The $\Delta\epsilon$ given is based on the concentration of the inorganic complex, unless otherwise noted. For the CD centered at ca. 300 only the longer wave maxima is given. ^{b} A saturated solution of 1 was used. ^{c} The $\Delta\epsilon$ is based on the concentration of the glycol. ^{d} The concentration of Ni(acac)$_2$ is approximate since it was added as a solid. ^{e} The enantiomer was in fact used. ^{f} Gift of Professor D. Horton, The Ohio State University. ^{g} Gift of Professor Y. Shimizu, University of Rhode Island.

differential CD (Figure 2), therefore, is due to complexation. (9, 10, 11) These compounds involve competition between two bidentate systems. Entry 9 consists of both an α- and β-glycol. The result obtained is that for the 1,3-glycol, presumably due to the fact that rotation of the primary OH allows these two hydroxyls to approach closer. In entries 10 and 11[5] the prim/sec amino alcohol complexes preferentially to that of the sec/sec because of the steric hindrance of the latter. A complex involving just the 1,3-glycol was ruled out since the relatively greater nucleophilicity of the amine should dominate. Finally, in all three cases opposite results would have been obtained if the alternative system were complexing.

(5) A recent publication reports the use of the Cupra-A method in the determination of the absolute configuration of some Chloramphenicol derivatives; see L. A. Mitscher, P. W. Howison, and T. D. Sokolski, *J. Med. Chem.*, **16**, 98 (1972).

The results mentioned clearly demonstrate the general applicability of this method.[6]

J. Dillon, K. Nakanishi*
*Department of Chemistry, Columbia University
New York, New York 10027*

Stabilization of σ-Delocalized Ions

Sir:

As has been pointed out[1] a 1-phenyl substituent enhances the rate of solvolysis of 2-*exo*-norbornyl deriva-

(1) H. C. Brown, F. J. Chloupek, and M. -H. Rei, *J. Amer. Chem. Soc.*, **86**, 1246 (1964).
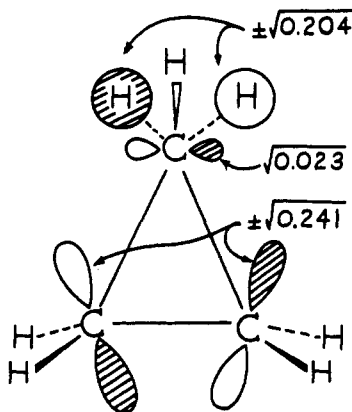
Figure 1. LUMO of corner protonated cyclopropane.

tives by a factor of only 6^2 in sharp contrast to the rate enhancement of $300,000,000^4$ provided by a 2-phenyl substituent. In view of the widely held assumption among organic chemists that the stabilization provided by a substituent should be essentially proportional to the charge developed at the site of substitution,[5] it is not surprising that these disparate factors have encouraged the conclusion that little charge was being developed at C_1 in the norbornyl transition state. With π-delocalized cations derived from alternant hydrocarbons (*e.g.*, allyl) the stabilization by methyl or phenyl is both expected and observed[6] to be nearly proportional to the charge anticipated from simple resonance arguments. With nonalternant cations (*e.g.*, cyclopropenyl[7,8]) and σ-delocalized ions,[9,10] much smaller stabilizations are observed. The aim of this communication is to point out that simple perturbation theory[11-13] provides both a qualitative insight into the source of this diminished substituent sensitivity and a semiquantitative expression of it.

If a substituent stabilization of a cation is thought of

as largely charge transfer between the uppermost filled orbital (HOMO) of the substituent and the lowest unoccupied orbital (LUMO) of the cation, changes in stabilization can be associated with changes in the second-order perturbation expression $\beta_{sc}^2/\Delta E$ (where β_{sc} is the resonance integral between the substituent HOMO and the cation LUMO and ΔE is the energy gap between the HOMO and the LUMO). Dewar[7,11] has discussed the influence of the ΔE term on substituent stabilization of nonclassical ions. Unlike simple π-cations the strong asymmetric mixing of levels of σ-delocalized ions gives LUMO's of elevated energy. The CNDO/2 calculations reported below indicate that stabilization of σ-delocalized ions is reduced by a factor of 0.5–0.8 as a result of this larger gap.

The β_{sc}^2 factor provides a greater diminution. The wave function for the LUMO of the parent corner protonated cyclopropyl cation (Figure 1) can be thought of as arising from the mixing of an antibonding orbital of a bent CH_3 cation with the antibonding π^* state a bent ethylene. Because of the intense mixing of these orbitals the coefficient representing p character at either CH_2 is reduced to less than 0.5 (compared to 1.0 for a methyl cation), giving rise to the energy reduction factor of about 0.24 for β_{sc}^2. The coefficients of the p orbitals of the other neighboring unoccupied MO's are even smaller. Combination of this with the Dewar energy gap factor accounts for the magnitude of the overall reduction of about 0.1–0.2 found experimentally and predicted in the calculations reported below. From this viewpoint what is important in determining substituent effects is not the gross atomic charges but the LUMO charges. These two charges are not in general equal. It follows that delocalization of charge as probed by substituent effects can give a misleading picture of the electronic structure of the ion.

Although many calculations are available in the literature for particular σ-delocalized ions[14] there does not appear to be a single set using a consistent set of parameters that can be used to test the perturbational treatment described above.[15] We report in Table I the substituent stabilizations of a series of methyl and phenyl substituted corner protonated cyclopropanes with appropriate reference compounds all calculated by the CNDO/2 model.[16] Energy changes for the hypothetical equilibrium

$$RCH_2^+ + CH_4 \rightleftharpoons RCH_3 + CH_3^+$$
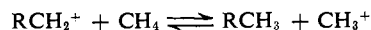
are recorded in column two, the changes for the equilibrium

$$RCH^+CH_3 + CH_3CH_3 \rightleftharpoons RCH_2CH_3 + CH_3CH_2^+$$

in column three, and the similar energy changes for a corner protonated cyclopropane in columns four and five. Substituent effects on a symmetrically bridged (C_{2v}) norbornyl cation have not been calculated al-

(2) The observed factor is 3.91. The value given corrects for the phenyl "inductive" effect as estimated from the phenyl substituent effect on the solvolysis of the *endo* norbornyl derivative.[3]

(3) P. v. R. Schleyer and D. C. Kleinfelter, Abstracts, 138th Meeting of the American Chemical Society, New York, N. Y., Sept 1960, No. 43P.

(4) H. C. Brown and M. -H. Rei, *J. Amer. Chem. Soc.*, **86**, 5008 (1964).

(5) For a recent example see H. C. Brown and E. N. Peters, *J. Amer. Chem. Soc.*, **95**, 2400 (1973), and its rebuttal by G. A. Olah and P. W. Westerman, *ibid.*, **95**, 7530 (1973).

(6) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; (b) "Molecular Orbital Theory for Organic Chemistry," Wiley, New York N. Y., 1961. Excellent recent reviews by Deno and by Sorenson may be found in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1972.

(7) M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.*, **16**, 321 (1965).

(8) R. Breslow, *J. Amer. Chem. Soc.*, **92**, 984 (1970), R. C. Kerber and C. -M. Hsu, *ibid.*, **95**, 3239 (1973), and references cited therein.

(9) R. A. Sneen, *et al.*, *J. Amer. Chem. Soc.*, **83**, 4843 (1961); P. v. R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

(10) C. F. Wilcox, Jr., R. G. Jesaitis, and S. Belin, Abstracts 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. ORGN 8. Other explanations of the small effect of a 1-phenyl substituent are reviewed by G. D. Sargent, *Quart. Rev., Chem. Soc.*, **20**, 301 (1966).

(11) (a) M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3341, 3345, 3350, 3353, 3357 (1952); (b) "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, and references therein.

(12) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952) and K. Fukui, *Forschr. Chem. Forsch.*, **15**, 1 (1970), and references therein.

(13) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(14) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969); L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **94**, 311 (1972); N. Bodor, M. J. S. Dewar, and D. H. Lo, *ibid.*, **94**, 5303 (1972); H. Kollmar and H. O. Smith, *Theor. Chim. Acta*, **20**, 65 (1971), and the many references cited in these papers.

(15) Since the original preparation of this manuscript Professor Schleyer has informed us of unpublished *ab initio* calculations with W. Hehre on methyl and phenyl substituted corner protonated cyclopropanes. Their numerical results appear to agree with the conclusions of this paper.

(16) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

Table I. Substituent Stabilization Energies,[a] eV

Substituent	Methyl cation	Ethyl cation	Corner protonated cyclopropane on >CH_2	Corner protonated cyclopropane on >CH_3
H–	0.0	0.0	0.0	0.0
CH_3–	3.21	2.20	0.44	–0.08
C_6H_5–	4.27[b] (3.65)[b]	3.84	0.45 (0.41)[c]	–0.12

[a] CNDO/2 energies. These energies refer to the gas phase and do not include the energy scaling factor of about one-third appropriate to this model. [b] The first entry is for a phenyl ring oriented with the p orbitals parallel to the empty p orbital of the cation. The entry in parentheses is for the perpendicular arrangement. [c] As in footnote b except that the parallel arrangement was defined to approximate maximum stabilization.

though the parent cation has been. The energy levels and wave functions of the norbornyl cation LUMO and nearby orbitals correspond closely to those for corner protonated cyclopropane so that the qualitative conclusions drawn above should apply to the norbornyl cation as well. On this basis, with the additional assumption that these gas phase cation energy reduction factors apply unaltered to experimental solvolysis data, substituent effects for 1-methyl- and 1-phenyl-substituted bridged cations can be estimated using a representative value of $^1/_6$ for the diminution factor.

Taking the substituent effect of a phenyl stabilization of simple[4,17] secondary acylic cations to be $10^{8.4}$, the bridged 1-phenylnorbornyl cation is estimated to be ca. $10^{8.4/6} = 10^{1.4} = 25$ (observed 6).[3] The analogous calculation for methyl gives an estimated rate of $10^{5/6} = 7$ (observed 45).[3] It is clear that these estimates of phenyl and methyl substituent effects do not give precise values but they do capture well the dramatic lowering of the substituent effect. The possible sources of the remaining discrepancy are many. Two outstanding candidates are nonlinear polarizability effects due to gegenion perturbations (CNDO/2 does not handle polarizability properly[18]) and variable solvation phenomena.[19] Other interpretations have been summarized by Sargent.[20]

A similar energy argument applies to the effect of para substituents on the 1-phenylnorbornyl solvolyses. It would be anticipated that the ρ for the exo series would be about ($^1/_6$) × (–4.5) (the ρ for t-cumyl chloride solvolyses) units more negative than the endo series. This is in reasonable accord with the available experimental evidence ($\rho_{exo} = -1.36$ and $\rho_{endo} = -1.06$ for tosylate acetolyses)[3] particularly when the possible variation in electrostatic field effects is considered.

In conclusion we feel that the perturbational model, although it can never be a substitute for an ab initio calculation, provides a useful insight into the basis for the observed substituent effects in σ-delocalized ions.

(17) Actually there is no unique value for phenyl stabilization, only a range of which the adopted value is near the upper limit; see particularly W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, J. Amer. Chem. Soc., 94, 133 (1972), and ref 11a.

(18) H. Meyer and A. Schweig, Theor. Chim. Acta, 29, 375 (1973).

(19) Schleyer for example (J. L. Fry, et al., J. Amer. Chem. Soc., 92, 2540 (1970)) has demonstrated with adamantyl derivatives that diminution of solvation leads to enhanced methyl substituent effects (from a typical 10^5 value to 10^8). Phenyl substituted adamantyl also shows a rate enhancement (see this paper for references) but not proportionately as much.

(20) G. D. Sargent in "Carbonium Ions," Vol. III, G. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1973.

It suggests further that the detailed pattern of the observed effects on norbornyl solvolyses not only does not preclude a bridged ion but possibly provides a diagnostic test for its intervention.[21,22]

(21) A very similar pattern of methyl and phenyl substituent effects is found for substituted phenonium for which there is substantial agreement that bridging is involved. See C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer, ref 20, Chapter 27.

(22) Similar calculations on the unbridged norbornyl cation suggest that substituents at C_6 should have a greater stabilizing effect than at C_1.

(23) (a) National Science Foundation Trainee, 1969–1973. (b) National Science Foundation Predoctoral Fellow, 1963–1967.

C. F. Wilcox, Jr.,* L. M. Loew,[23a] R. G. Jesaitis[23b]
S. Belin, J. N. C. Hsu
Department of Chemistry, Cornell University
Ithaca, New York 14850
Received August 13, 1973

Homogeneous Catalysis of Aromatic Hydrocarbon Hydrogenation Reactions

Sir:

We report the first unequivocal demonstration of catalysis of aromatic hydrocarbon hydrogenations with a discrete metal complex.[1] Hydrogenation occurs under mild conditions with η^3-allylcobalt phosphite[2] catalysts.

Hydrogenation of benzene to cyclohexane proceeded at a low rate at 25° and <760 mm; a total of about 20 catalyst cycles were achieved within 48 hr with η^3-C_3H_5-Co[P(OCH$_3$)$_3$]$_3$.[3] Hydrogenation rate is an order of magnitude higher in polar media.[4] Examination of the pale orange reaction solutions with oblique light gave no evidence of the presence of solids, and spectroscopic data indicated the absence of paramagnetic solids.[5] Olefins, cyclohexene included, were hydrogenated with this catalyst.

Considerable scope is evident in this new homogeneous catalytic reaction. Alkylbenzenes are converted to alkylcyclohexanes, anisole to methoxycyclo-

(1) There are many claims to homogeneous catalysis of aromatic hydrocarbon hydrogenations; however, the demonstration of such catalysis by a discrete metal complex has not to our knowledge been demonstrated. Khidekel' and coworkers have described an amorphous black rhodium complex with phenylanthranilic acid which gives a black reaction mixture that catalytically hydrogenates benzene. Molecularity and homogeneity were not uniquely defined: V. A. Avilov, Yu. G. Borod'ko, V. B. Panov, M. L. Khidekel', and P. S. Chekrii, Kinet. Katal., 9, 582 (1968); O. N. Efimov, O. N. Eremenko, A. G. Ovcharenko, M. L. Khidekel', and P. S. Chekrii, Bull. Acad. Sci. USSR, Div. Chem. Sci., 778 (1969); O. N. Efimov, M. L. Khidekel', V. A. Avilov, P. S. Chekrii, O. N. Eremenko, and A. G. Ovcharenko, J. Gen. Chem. USSR, 38, 2581 (1968). Lapporte (S. J. Lapporte, Ann. N. Y. Acad. Sci., 158, 510 (1969); S. J. Lapporte and W. Schuett, J. Org. Chem., 28, 1947 (1963)) reports the hydrogenation of arenes with black, uncharacterized reaction mixtures of organic transition metal carboxylates reduced with trialkylaluminum at relatively extreme conditions of temperature (150–210°) and pressure (~70 atm).

(2) E. L. Muetterties and F. J. Hirsekorn, J. Amer. Chem. Soc., 95, 5419 (1973).

(3) (a) Cyclohexene, identified by gas chromatographic and mass spectrometric analysis, was evident only in reaction systems that contained a deficiency of hydrogen and even in these instances the ratio of C_6H_{10} to C_6H_{12} was less than 1:10. (b) Rate of reaction at higher temperatures and pressures has not been established as yet. Initially all reactions were carried out under modest conditions in glass equipment in order that we could ensure that truly homogeneous catalytic reactions were being observed. We have examined typical, coordinately unsaturated catalysts, like ClRh[P(C$_6$H$_5$)$_3$]$_3$, and found no hydrogenation under our conditions.

(4) Rate of catalyst degradation is also elevated. Normally the arene was not diluted with a solvent.

(5) This characterization is rigorously correct for at least the first 24 hr of reaction.