

Table I. Substituent Stabilization Energies,^a eV

Substituent	Substituted cation		
	Methyl cation	Ethyl cation	Corner protonated cyclopropane on >CH ₂ on >CH ₃
H-	0.0	0.0	0.0
CH ₃ -	3.21	2.20	0.44
C ₆ H ₅ -	4.27 ^b (3.65) ^b	3.84	0.45 (0.41) ^c

^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 acyclic cations to be $10^{3.4}$, the bridged 1-phenylnorbornyl cation is estimated to be *ca.* $10^{3.4/6} = 10^{1.4} = 25$ (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 properly¹⁵) 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 $(1/6) \times (-4.5)$ (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 10^3 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 C₅ should have a greater stabilizing effect than at C₁.

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

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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 phosphite² 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 -C₃H₅-Co[P(OCH₃)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).

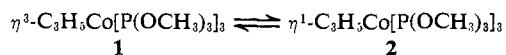
(3) (a) Cyclohexene, identified by gas chromatographic and mass spectrometric analysis, was evident only in reaction systems that contained a deficiency of hydrogen and even in these instances the ratio of C₆H₁₀ to C₆H₁₂ was less than 1:10. (b) Rate of reaction at higher temperatures and pressures has 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(C₆H₅)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.

hexane, and ethyl benzoate to ethyl cyclohexenylcarboxylate. Selectivity in the last case seems to be a steric or a kinetic effect due to conjugative stabilization⁶ in the unsaturated ester. Hydrogen exchange through CoH-CH reactions is not significant in the catalytic sequence because perdeuteriobenzene yielded only C₆H₆D₆.⁷ There is stereoselectivity in this catalytic reaction since *m*-xylene was converted to *cis*-1,3-dimethylcyclohexane and *o*-xylene to *cis*-1,2-dimethylcyclohexane. A clear indication of steric encumbrances in the hydrogenation reaction was the very low rate of reaction with mesitylene at 25° to give *cis,cis*-1,3,5-trimethylcyclohexane. The aromatic ring in furan is also reduced to yield tetrahydrofuran.

We confidently presume that the first step in the catalytic hydrogenation is an $\eta^3 \rightleftharpoons \eta^1$ conversion⁸ to yield a coordinately unsaturated complex 2



Confirmatively, we found that 1 reacts far faster with CO to give carbonyl derivatives than do HCo[P(OCH₃)₃]₄ and CH₃Co[P(OCH₃)₃]₄ which ostensibly must dissociatively lose a phosphite ligand before CO reaction may occur.⁹ Subsequent to the $\eta^3 \rightleftharpoons \eta^1$ reaction would be oxidative addition of hydrogen¹⁰ to 2 to give $\eta^1\text{-C}_6\text{H}_5\text{CoH}_2\text{[P(OCH}_3)_3]_3$ (3). This addition of hydrogen was tentatively indicated in reaction of 1 with hydrogen in a pyridine and in an acetonitrile solution; neither solvent was hydrogenated. Nmr spectroscopic studies of 1 in nonpolar and polar solvents under hydrogen pressure, in fact, showed an allyl proton nmr resonance that can be interpreted in terms of a η^1 allyl ligand, as in 3, but a metal hydride resonance for the putative hydride has not yet been detected. We fully expected to see rapid elision of the allyl group in 3 by proton transfer to give propylene and a coordinately unsaturated HCo[P(OCH₃)₃]₃ (4) and further expected 4 to be the active catalyst. Actually, we found no evidence of 4 although this species may be present in very low concentrations. Essentially complete recovery of 1 from hydrogenation reactions was realized when the reaction time did not exceed ~24 hr. After reaction times of several days, the hydrogenation rate fell sharply due to catalyst destruction; and, in these instances, 1, HCo[P(OCH₃)₃]₄, and free phosphite¹¹ were detected in addition to a small amount of paramagnetic solid.

The geometric mode of initial arene attachment to the cobalt center is probably "over an edge."¹² This in-

(6) No ethyl cyclohexylcarboxylate was detected. Some cyclohexane is formed which suggests that the rate of hydrogenation of the cyclohexenylcarboxylate is substantially lower than reductive cleavage of the carboxylate in the cyclohexyl derivative.

(7) This was the only species detected within the limits of the gas chromatographic and mass spectrometric analysis procedure. The stereochemistry has not as yet been unequivocally established.

(8) The rate of this process is low with respect to the nmr time scale.²

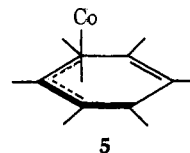
(9) E. L. Muetterties and F. J. Hirsekorn, to be submitted for publication.

(10) Oxidative addition of hydrogen to coordinated unsaturated complexes is a well-established reaction and, in fact, has been reported for cobalt(I) complexes. For general and specific references, cf. E. L. Muetterties, "Transition Metal Hydrides," Marcel Dekker, New York, N. Y., 1971, Chapters 5 (pp 210 and 211) and 6.

(11) Free phosphite ligand is an expected hydrogenation reaction inhibitor.

(12) This would be analogous to a quasi olefin complex. Certainly intermediates of this general form must be involved in the sequential reaction steps of metal hexacarbonyls with aromatic hydrocarbons, where η^6 -arene complexes are the ultimate products.

teraction would be followed by hydrogen migration to give a cyclohexadienylcobalt complex. Further hydrogen transfer would then yield cyclohexadiene by reductive elimination. Cyclohexadiene, and the next intermediate cyclohexene, *might* then compete more effectively than the arene in further sequences to preferentially give, as observed, cyclohexane. Alternatively an η^3 -cyclohexadienyl complex, 5, might be an



intermediate. In any case, the stereochemical character of an η^2 -olefin or η^3 -cyclohexadienyl complex must be such that methyl substituents are always preferentially directed away from the cobalt center to account for the stereoselective formation of *cis*-polyalkylcyclohexanes from *o*- and *m*-xylene and mesitylene.

All plausible mechanistic schemes would seem to require phosphite ligand dissociation. We find that polar media like alcohols and nitriles raise the rate of phosphite ligand dissociation¹³ and the rate of the hydrogenation reaction. This ligand dissociation step might be rate determining in the hydrogenation reaction. However, the $\eta^3 \rightleftharpoons \eta^1$ interconversion may also be a significant rate limiting step. Donor molecules or ligands are known to promote $\eta^3 \rightleftharpoons \eta^1$ processes in allylmetal complexes.¹⁴

We are presently attempting synthesis of model structures, like HCo[P(OCH₃)₃]₃, η^3 - or η^1 -C₆H₇Co[P(OCH₃)₃]_x (*x* = 3 or 4), and RCoH₂[P(OCH₃)₃]₃, that are or that emulate the possible intermediates in this catalytic hydrogenation in order that the hydrogenation reaction might be logically extended to other classes of aromatic hydrocarbon reactions. We consider these findings as an important first step in the generation of a broad range of homogeneous catalytic reactions of aromatic and aliphatic hydrocarbons; hydrocyanation and hydroformylation of arenes are realistic extensions.

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(13) This phenomenon has been observed for HCo[P(OCH₃)₃]₄ and for the allyl complex.³

(14) K. Vrieze, C. MacLean, P. Cossee, and C. W. Hilbers, *Recl. Trav. Chim. Pays-Bas*, **85**, 1077 (1966); *J. Organometal. Chem.*, **6**, 672 (1966).

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Photochemical Synthesis of a 1,8-Naphthoquinodimethane, Generation of a Thermally Accessible Triplet

Sir:

In a previous communication,¹ the thermolysis of 1 was described. By studying the decomposition of 1a and 1b under a wide variety of conditions, it was con-

(1) R. M. Pagni and C. R. Watson, Jr., *J. Amer. Chem. Soc.*, **96**, 2291 (1974).