Table I. Extent of Rearrangement of Phenylacetylene-1-^{13}C and Phenylacetylide-1-^{13}C Anion

Entry	Base	Solvent	Temp, °C	Time, hr	% 1-^{13}C Initial	% 1-^{13}C Final
1	None	Benzene	178 ± 5	4.1	56.0[a]	56.0
2	$NaNH_2$[b]	THF[c]	65 ± 1	17.5	56.0	~56
3	$NaNH_2$	THF	160 ± 2	2.0	32.6	32.0[d]
4	KOBu-*t*	*t*-BuOH	130 ± 2	1.5	32.3	32.3
5	$LiNHC_6H_{11}$	*c*-$C_6H_{11}NH_2$	160 ± 1	2.0	32.6	32.3[d]

[a] All values are calculated from several integrations of the ^{1}H nmr and are ±~2%. [b] The ratio of base:phenylacetylene in all cases was 2:1 or 3:1. [c] Several milliliters of solvents per millimole of phenylacetylene. [d] However, mass spectral analysis of carbon dioxide obtained from the permanganate oxidation [V. N. Krestinskii and M. K. Kelbovskaya, *Ber.*, **68B**, 512 (1935)] of phenylacetylene recovered from runs 3 and 5 showed 2.62 ± 0.14% ^{13}C and 1.60 ± 0.12% ^{13}C, respectively. Since a control sample showed 2.34 ± 0.80% ^{13}C, the extent to which these results represent carbon skeleton rearrangement rather than excessive oxidation is not known.

$$Ph^{13}CO_2H \xrightarrow{SOCl_2} Ph^{13}COCl \xrightarrow{Me_2Cd} Ph^{13}COMe \qquad (5)$$

$$Ph^{13}COMe \xrightarrow{PCl_5} Ph^{13}CCl_2CH_3 + Ph^{13}CCl{=}CH_2 \xrightarrow{NaNH_2} Ph^{13}C{\equiv}CH \qquad (6)$$

elsewhere.[5] Isotopic analysis of samples of enriched phenylacetylene was carried out using the $^{2}J_{^{13}\mathrm{CCH}}$[6a] and the $^{1}J_{^{13}\mathrm{CH}}$[6a,b] coupling, by ^{1}H nmr, both before and after attempted rearrangement of the anion. Isolation of phenylacetylene was accomplished by hydrolysis and extraction or by precipitation of the insoluble silver phenylacetylide.

Both phenylacetylene-1-^{13}C and the anion produced therefrom by three different bases in solvents of disparate polarity maintained their isotopic integrity even under the most severe conditions which would still permit recovery of a practical amount of phenylacetylene. The results are summarized in Table I. Using the data from entries 3 and 5 of Table I and making the reasonable[7] assumption that $\Delta S^{\neq} \cong 0$ and that first-order kinetics would prevail for this rearrangement, it is possible to calculate a value for $\Delta H^{\neq}$ (minimum) of 37.4 kcal/mol for the rearrangement. This result fully supports the theoretical conclusion of Hoffmann that the activation energy for this rearrangement should be highly unfavorable.[8]

Acknowledgment. The authors are indebted to the National Science Foundation and to California State College, Los Angeles, for financial support of this work.

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(5) J. Casanova, Jr., and R. N. Morris, "Organic Preparations and Procedures," in press.

(6) (a) P. C. Lauterbur in "Determination of Organic Structures by Physical Methods," Vol 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, Chapter 7; (b) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).

(7) Kohlmaier and Rabinovitch[2a] have determined $\Delta S^{\neq} = -4.8$ eu for the gas-phase rearrangement of *p*-tolyl isocyanide, and have suggested a somewhat higher value for the solution reaction.

(8) Van Dine and Hoffmann[3] have calculated $\Delta H^{\neq} = 58$ kcal/mol for this reaction.

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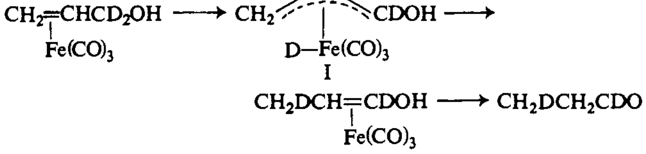
The Mechanism of Iron Pentacarbonyl Catalyzed 1,3-Hydrogen Shifts

Sir:

Several examples have recently been reported[1] which indicate that electrocyclic and cycloaddition transformations which are symmetry "forbidden" by the Woodward–Hoffmann rules[2] become "allowed" when the reaction is catalyzed by various transition metal complexes. An explanation for the contradictory behavior of systems catalyzed by metals has been given by Pettit[1a] and Mango and Schachtschneider.[1c] In essence, it is concluded that interaction of appropriate metal orbitals with those of the olefin forms a new set of occupied molecular orbitals which provide a symmetry-allowed reaction pathway.

Concerted, thermally induced, sigmatropic hydrogen shifts of order [1,3] are "allowed" to proceed only *via* the sterically unfavorable antarafacial mode,[2a] and it is significant that no such migrations have been reported. However, 1,3-hydrogen shifts brought about by the influence of a metal catalyst could conceivably occur through the sterically favorable suprafacial pathway since back donation[3] of metal d electrons to the olefinic ligand could result in a molecular orbital of proper symmetry being the highest occupied one. Such a process would then be analogous to the photochemical process where such 1,3-hydrogen shifts have been reported.[2a] Indeed, it has been suggested[1c] that such a process is operative in the $DCo(CO)_4$-catalyzed isomerization of allylbenzene to β-methylstyrene[4] since only about 5% deuterium was found to be incorporated in the product.

We have previously reported the occurrence of a 1,3-hydrogen shift in the $Fe(CO)_5$-induced isomerization of allyl alcohol to propionaldehyde.[5] Thus, rearrangement of [1,1-$^2H_2$]allyl alcohol with $Fe(CO)_5$ produced propionaldehyde with deuterium appearing in the methyl but *not* in the methylene group. Similar results have been reported in the rearrangement of allyl alcohol with $DCo(CO)_4$.[6] Our results were found to be consistent with the rearrangement proceeding *via* a π-allyl–hydroiron tricarbonyl complex (I), as had been suggested earlier by Pettit[7] and Manuel.[8] However, the data are



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(1) (a) W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **89**, 4788 (1967); (b) H. Hogeveen and H. C. Volger, *ibid.*, **89**, 2486 (1967); (c) F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2484 (1967), and references therein.

(2) (a) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395, 2511, 4389 (1965), and references therein; (b) *ibid.*, **87**, 2046 (1965); (c) *ibid.*, **87**, 4388 (1965); (d) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965); (e) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (f) J. A. Berson, *ibid.*, **1**, 152 (1968); (g) G. B. Gill, *Quart. Rev.* (London), **22**, 338 (1968).

(3) M. J. S. Dewar, *Bull. Soc. Chim. France*, **18c**, 79 (1951).

(4) L. Roos and M. Orchin, *J. Am. Chem. Soc.*, **87**, 5502 (1965).

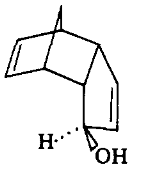
(5) W. T. Hendrix, F. G. Cowherd, and J. L. von Rosenberg, *Chem. Commun.*, 97 (1968).

(6) R. W. Goetz and M. Orchin, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

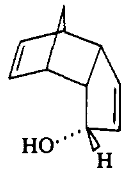
(7) G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962).

consistent also with the hydrogen migration occurring through a concerted, suprafacial pathway not requiring the intermediacy of I.

No evidence has been reported to date which allows a distinction to be made between the two mechanisms. We wish now to report the results of experiments designed to make this distinction.



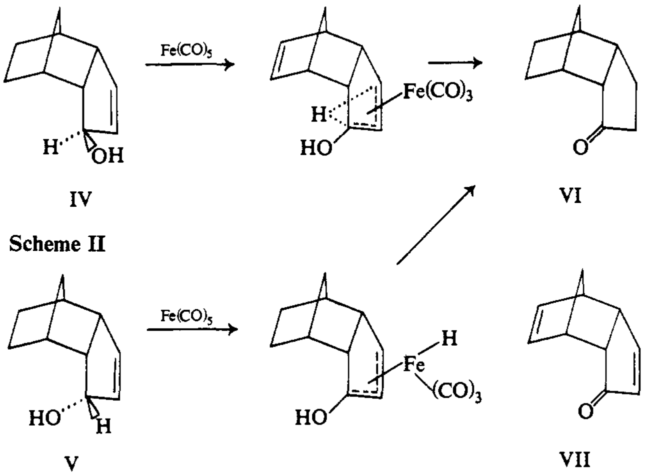
II



III

endo-α-1-Hydroxydicyclopentadiene (II) and *endo*-β-1-hydroxydicyclopentadiene (III) were prepared from *endo*-dicyclopentadiene by the method of Woodward and Katz.[9] These were converted to the corresponding *endo*-α-1-hydroxy-5,6-dihydrodicyclopentadiene (IV) and *endo*-β-1-hydroxy-5,6-dihydrodicyclopentadiene (V) by catalytic hydrogenation in the presence of a palladium on charcoal catalyst, a method known to selectively saturate the strained double bond in this tricyclic ring system.[10] Compounds IV and V were shown to be epimers by the fact that stirring an acetone solution of V with dilute HCl at room temperature produced a mixture consisting of only IV (*ca.* 60%) and V (*ca.* 40%).[11]

Scheme I



IV VI

Scheme II

V VII

Schemes I and II illustrate the essentials of the two possible mechanisms. In both schemes, only approach of $Fe(CO)_5$ from the least hindered *exo* side is reasonable. In fact, reduction of 5-6-dihydrodicyclopentadien-1-one (VII) with $NaBH_4$ gave a 9:1 ratio of V to IV.

As shown in Scheme I rearrangement of IV to tetrahydrodicyclopentadien-1-one (VI) would be expected to occur only if a 1,3-suprafacial hydrogen shift is operative. In this case, the migrating hydrogen is clearly not properly positioned to allow the formation of a π-allyl–hydroiron tricarbonyl complex. However, a concerted suprafacial 1,3-hydrogen shift would be expected to proceed without any obvious restraints.

Scheme II illustrates the isomerization of the β-alcohol V proceeding to VI *via* a π-allyl–hydroiron tricarbonyl complex. In V, the migrating hydrogen is in a favorable position to allow its facile transfer to the iron, and for any rearrangement to occur *some mechanism involving iron–hydrogen bonding is required.*

Compound V was found to isomerize to ketone VI in about 40% yield when heated at 130° for 16 hr with 10 mole% $Fe(CO)_5$ under a N_2 atmosphere. In contrast, however, under the same conditions and, even with prolonged heating at 160°, compound IV *exhibited no detectable change.*[11b]

Our findings definitely indicate that isomerizations of unsaturated alcohols, and quite likely other similar olefin transformations, brought about by reaction with $Fe(CO)_5$ require a definite stereochemical relationship between the migrating hydrogen and the iron atom. A mechanism involving a π-allyl–hydroiron tricarbonyl complex is compatible with these results, while a concerted, sigmatropic hydrogen shift of order [1,3] involving no hydrogen–iron bonding is not. However, a mechanism involving a suprafacial 1,3-hydrogen shift occurring on the same face as the metal atom is also possible. This need not involve a discrete Fe–H intermediate, but the transition state could resemble a cyclobutadiene–metal type interaction. Such a transition state would be isoconjugate with cyclobutadiene metal complexes according to Dewar's concepts of the energetics of the allowed Woodward–Hoffmann processes.[12]

Acknowledgment. The authors are grateful to the National Science Foundation for financial support of this work.

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[8] T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

[9] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[10] K. Alder and G. Stein, *Ann. Chem.*, **485**, 223 (1931); T. J. Katz, M. Rosenberger, and R. K. O'Hara, *J. Am. Chem. Soc.*, **86**, 249 (1964).

[11] (a) This analysis and subsequent product analyses were determined by gas-liquid partition chromatography. (b) The lower limit of detectability of VI by this method was found to be less than 0.1%.

[12] Professor M. J. S. Dewar, personal communication; M. J. S. Dewar, "Aromaticity," Special Publication No. 21, The Chemical Society, London.

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A Double Consecutive Inversion at Two Nitrogens in a Heterocyclic Diamine. The Conformational Isomerization of N,N′-Di-*t*-butylpiperazinium Dichloride

Sir:

The ring inversion, I_R, of an N,N′-dialkylpiperazine[1] causes the methylenic protons and the N substituents R to exchange their axial and equatorial positions (E_C and E_N exchanges, respectively), while a nitrogen inversion, I_N, without ring distorsion, brings about E_N only (Figure 1, eq 1 and 2). An alternative (likely to account also for

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[1] L. W. Reeves and K. O. Stromme, *J. Chem. Phys.*, **34**, 1711 (1961); R. K. Harris and R. A. Spragg, *Chem. Commun.*, 314 (1966); *J. Chem. Soc., B*, 684 (1968).