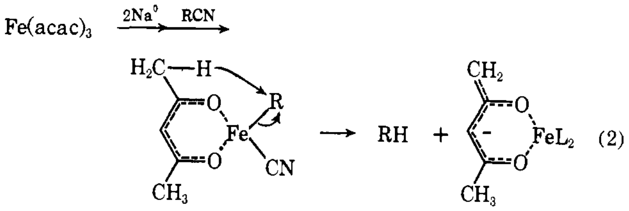
dry benzene at room temperature for 50–70 hr. After the addition of 0.5 ml of water, the reaction mixture was analyzed for hydrocarbon content by vpc means (10 ft long, $^1/_4$ in. Porapak S or 10% Carbowax column at 100–120°). It is of interest that the best yields (58–100%) are obtained with saturated primary, secondary, and tertiary cyanides. The lower yields (40–46%) observed in the allyl and phenyl cases may be a consequence of alternative behavior patterns of the more stable allyl and phenyl radicals. Yields (per cent) of *n*-octane from *n*-octyl cyanide decreased markedly when the same, or a similar, procedure was employed, but with different transition metal–reducing agent combinations, *e.g.*: $TiCl_3$–Mg (2.5), $FeCl_3$–Mg (5), $CoCl_2$–Mg (3.5), Ti(O-*i*-$C_3H_7)_4$–K (25), Fe(acac)$_3$–Mg (0.0–0.5), Fe(acac)$_3$–Zn(0). With Mo(acac)$_3$–Na or NaNp, yields for the octyl cyanide case fell in the range 14–71%. Reductive decyanations with "titanocene" ($C_{20}H_{20}Ti_2$) (in toluene for 2 days at room temperature) are noteworthy in that although yields in preliminary experiments were lower than with the Fe(acac)$_3$–Na system, no external reducing agent need accompany the transition metal reagent.[3]

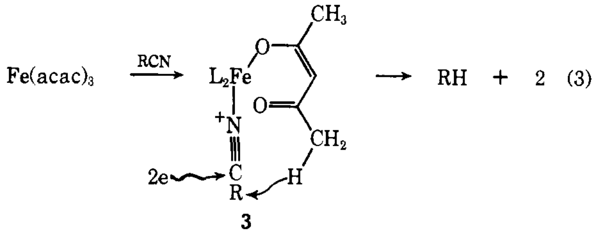
In connection with stoichiometric and mechanistic aspects, the following experiments were carried out. A series of reduction runs, in which the molar ratios of Fe(acac)$_3$ or metallic sodium were varied while other variables were held constant, revealed that 1 and 2 equiv, respectively, of these reagents are required for maximal yields of hydrocarbon product. Considerably decreased yields resulted when either Fe(acac)$_3$ was omitted from the reaction, or the sodium sand was allowed to stand in contact with the Fe(acac)$_3$ solution for 70 hr before starting nitrile was added. Although the exact fate of the transition metal reagent was not determined, the iron seemed to end up in the III state (red-reddish brown reaction solutions), while cyanide ion could be detected as silver cyanide on neutralization of the reaction product with dilute nitric acid. When benzene-d_6 replaced benzene-h_6 in a Fe(acac)$_3$–Na reduction of *n*-octyl cyanide, no incorporation (mass spectrum) of deuterium into the product *n*-octane could be detected. Since all of the *n*-octane is available *per se* at the end of the reduction reaction and before any proton source is added, the hydrogen incorporated into the alkane must derive from the Fe(acac)$_3$ reagent.[4] On the basis of the foregoing, an overall equation such as (1) would apply.

$$\mathrm{RCN + Fe(C_5H_7O_2)_3 + 2Na \longrightarrow RH + Fe(C_5H_7O_2)_2C_5H_6O_2^- + CN^- + 2Na^+} \quad (1)$$

The mechanism of the reduction might involve (a) oxidative addition of organic cyanide to an initially formed lower valent iron species,[5] giving *e.g.*, **1**, followed by proton transfer from the acac ligand to the organometallic moiety, thereby generating hydrocarbon (eq 2), or (b) initial coordination of nitrile with iron, generating, *e.g.*, **3**, followed by reductive cleavage of the nitrile 1,2 carbon–carbon bond, and proton transfer to the latter area (eq 3). Similarly, in the titanocene version, oxidative addition to the starting Ti(II) species would occur, but completion of the reaction would be achieved merely by supply of hydrogen to the alkyl residue from solvent or from a cyclopentadienide unit.[6]



1 **2**



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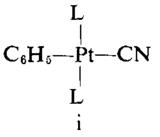
[3] An active form of titanocene was prepared, using the method of J. J. Salzman and P. Mosimann, *Helv. Chim. Acta*, **50**, 1831 (1967), and used *in situ* after removal by filtration of insoluble by-products.

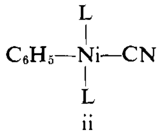
[4] That Fe(acac)$_3$ serves as more than a proton source in the reductive decyanation reaction is indicated by the finding that Al(acac)$_3$ does not increase the yield of octane from octyl cyanide beyond the level observed with metallic sodium alone.

[5] For oxidative additions of benzonitrile to Pt(0) and Ni(0) species to yield products i and ii, see J. L. Burmeister and L. M. Edwards,



$$C_6H_5\text{—}\overset{\displaystyle L}{\underset{\displaystyle L}{Pt}}\text{—}CN$$

i



$$C_6H_5\text{—}\overset{\displaystyle L}{\underset{\displaystyle L}{Ni}}\text{—}CN$$

ii

J. Chem. Soc. A, 1663 (1971); D. H. Gerlack, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 3543 (1971).

[6] H. H. Brintzinger and J. E. Bercaw, *ibid.*, **92**, 6182 (1970).

Oxidations of Hydroaromatic Systems. I.[1] The Oxidation of Tropilidene by Ceric Ammonium Nitrate

Sir:

The relative reactivities of oxidants toward carbon–hydrogen and carbon–carbon double bonds determine the course of hydrocarbon oxidations. Ceric ammonium nitrate (CAN) is known to oxidize toluenes in the side chain[2] in preference to reacting with the π-electron system of the aromatic ring. The purpose of our study was to examine whether CAN could also react with a carbon–hydrogen bond in preference to a nonaromatic unsaturated system.

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[1] (a) Support of this work by the U. S. Army Research Office–Durham is gratefully acknowledged. (b) Presented in part at the Third Great Lakes Regional Meeting of the American Chemical Society, DeKalb, Ill., June 1969.

[2] (a) W. S. Trahanovsky and L. B. Young, *J. Org. Chem.*, **31**, 2033 (1966); (b) R. Ramaswamy, M. S. Venkatachalapathy, and H. V. K. Udupa, *Bull. Chem. Soc. Jap.*, **35**, 1751 (1962); (c) L. A. Dust and E. W. Gill, *J. Chem. Soc. C*, 1630 (1970); (d) L. Syper, *Tetrahedron Lett.*, 4493 (1966).

Vincow, Dauben, Hunter, and Volland[3] recently made a detailed analysis of the resonance stabilization of the cycloheptatrienyl (tropenyl) radical $C_7H_7\cdot$ and of the cycloheptatrienyl (tropenium) cation $C_7H_7^+$. They concluded that the total resonance energy (RE) for the tropenyl radical is 31 kcal/mol of which 10 kcal/mol represents the RE of the cycloheptatriene system and 21 kcal/mol the "extra" RE due to the delocalization of the unpaired electron. As a result of the unexpectedly large resonance stabilization, the carbon–hydrogen bond in the methylene group of cycloheptatriene is considerably weakened; the bond dissociation energy is only 73 kcal/mol which is considerably lower than the bond dissociation energy for a carbon–hydrogen bond in a methylene group of a saturated hydrocarbon (94.5 kcal/mol),[4] in the methyl group of toluene (85 kcal/mol),[4] or even in the methylene group of 1,4-pentadiene[5] (79 kcal/mol). The oxidation of cycloheptatriene to the tropenyl radical by direct hydrogen atom abstraction should, therefore, be a favored process.

The tropenium cation has been recognized as an aromatic system for a long time.[6] Its "extra" resonance energy has a value of 49 kcal/mol.[3] The direct oxidation involving a hydride ion transfer should therefore be a particularly favorable process.[7] Although cerium(IV) reacts typically as a one-electron oxidant, two-electron oxidations leading to carbonium ions have been considered.[2a] Due to the large additional resonance energy which would be released in a hydride ion as compared with a hydrogen atom transfer, the two-electron mechanism should be particularly favored in the oxidation of cycloheptatriene.

Cycloheptatriene thus presents a compound uniquely suited for the testing of an oxidant's ability to react with a carbon–hydrogen bond in preference to a carbon–carbon double bond and was therefore selected for our study. Moreover, Trahanovsky and coworkers in a recent detailed investigation of the CAN oxidation of cycloheptatriene[8,9] convincingly demonstrated the formation of a tropenium ion intermediate.

The most important result of our study (Table I) is the complete absence of any kinetic isotope effect in the oxidation of cycloheptatriene-d_8.[10] This result clearly rules out any mechanism in which a carbon–hydrogen bond is broken in the rate-limiting step. Thus, in spite of the large resonance stabilization available for the transition state for the hydrogen atom or hydride ion abstraction, neither of these reactions takes place. *Thus, CAN obviously will not react even with a very reactive carbon–hydrogen bond of a hydrocarbon in preference to a nonaromatic carbon–carbon double bond.*

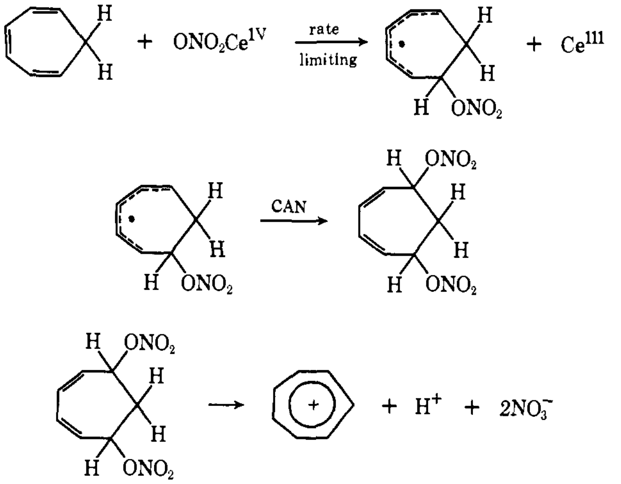
Table I. Rates of Olefin Oxidation by Ceric Ammonium Nitrate[a]

Olefin	$10^2 \times k_2$, M^{-1} sec^{-1}	k_{rel}
Cyclooctatetraene	1530	850.0
Cycloheptatriene[b]	372	205.0
Cycloheptatriene-d_8[b]	378	210.0
1,3-Cyclooctadiene	38.7	22.0
Norbornadiene	9.64	5.4
1,5-Cyclooctadiene	5.82	3.3
Cyclopentene	2.12	1.1
Cyclohexene	1.80	1.0
Cycloheptene	1.55	0.85

[a] Rates were determined spectrophotomatically at 350 nm (96% acetonitrile, 25°, $[HNO_3] = 1.00 \times 10^{-2}$ M, $[Ce(IV)]_0 = 5.3 \times 10^{-5}$ M). Good straight-line plots over two or three half-lives were obtained for the more reactive hydrocarbons. Substrate concentration 2×10^{-4}–10^{-2}. [b] The values are averages of four sets of measurements. The two compounds were measured alternately under identical conditions; the standard deviation for each compound was 2.5%.

The relative reactivities of the several unsaturated hydrocarbons given in Table I allow additional conclusions to be drawn about the mechanism of the CAN oxidation of cycloheptratriene. It will be noted that while all monoolefins and nonconjugated dienes react with comparable rates, the oxidation rates increase rapidly with the number of conjugated double bonds. Of particular significance is the high reactivity of cyclooctatetraene. We believe that the observed dependence of the oxidation rate on the number of conjugated double bonds is best accounted for by a mechanism in which the oxidant in the rate-limiting step attacks the end of the conjugated system with the formation of a delocalized free radical. The radical must then undergo further oxidation to the tropenium ion. Scheme I represents a plausible reaction sequence for the oxidation of cycloheptatriene to the tropenium ion. A ligand transfer of a NO_3 group is suggested to take place in the rate-limiting step.[11,13]

Scheme I



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(3) G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *J. Amer. Chem. Soc.*, **91**, 2823 (1969).

(4) (a) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); (b) S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965).

(5) K. W. Egger and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 241 (1966).

(6) *Cf.* A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1966.

(7) P. Müller and J. Roček, *J. Amer. Chem. Soc.*, in press.

(8) W. S. Trahanovsky, L. B. Young, and M. D. Robbins, *ibid.*, 91, 7084 (1969).

(9) W. S. Trahanovsky, M. D. Robbins, L. Van Roekel, and L. B. Young, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. ORGN 68.

(10) P. Müller and J. Roček, *J. Org. Chem.*, **33**, 3001 (1968). We preferred to use the perdeuterio compound instead of the 7,7-dideuterio-1,3,5-cycloheptatriene to avoid any complications or ambiguities from possible intramolecular hydrogen migration under the reaction conditions.

(11) Ligand transfer from CAN to substrates has been suggested earlier in the oxidation of free radicals.[12]

(12) (a) W. S. Trahanovsky and J. Cramer, *J. Org. Chem.*, **36**, 1890 (1971); (b) K. Meyer and J. Roček, *J. Amer. Chem. Soc.*, in press.

(13) A referee suggested that the rate-limiting formation of the free-radical $C_7H_8NO_3\cdot$ could be followed by electron-transfer oxidation to

The absence of an isotope effect could also be interpreted in terms of a rate-limiting formation of a complex between the hydrocarbon and the oxidant or of a rate-limiting electron-transfer reaction. We do not believe that any of these alternative mechanisms offer a better rationalization of the experimental data. Rate-limiting complex[14] formation would be difficult to reconcile with the high reactivity of cyclooctatetraene as compared with norbornadiene.

The reaction obviously follows a path energetically more favorable than that of the hydrogen atom abstraction which would require 73 kcal/mol. In the gas phase, electron abstraction leading to the radical ion $C_7H_8^+$ would require a considerable energy (197 kcal/mol).[15] Judging from the values for solvation enthalpies of singly charged ions of comparable size,[16] one could not expect that solvation could lower the energy needed to remove an electron by more than 70 kcal/mol. Hydrogen atom transfer to the oxidant or electron transfer with simultaneous transfer of a proton to the solvent (both cases would give rise to an isotope effect) would thus still be favored by more than 50 kcal/mol over rate-limiting electron transfers to give $C_7H_8^+$.

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the carbonium ion $C_7H_8NO_3^+$, which, upon loss of a proton and nitrate ion, would yield the tropenium ion. While this mechanism would satisfactorily account for the results repeated in the present study, it seems less attractive in the light of our recent observation that CAN reacts with free radicals preferentially by ligand transfer rather than by electron transfer.[12b]

[14] Reversible complex formation could of course precede the oxidation step.

[15] R. W. Kiser, "An Introduction to Mass Spectrometry and its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 310.

[16] D. F. C. Morris in "Structure and Bonding, Vol. 4," C. K. Jørgensen and J. B. Neilands, Ed., Springer-Verlag, New York, N. Y., 1968, p 63.

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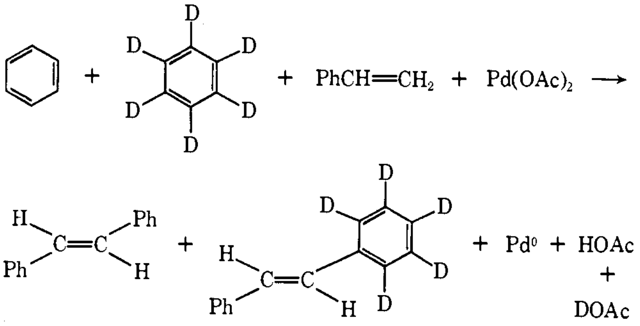
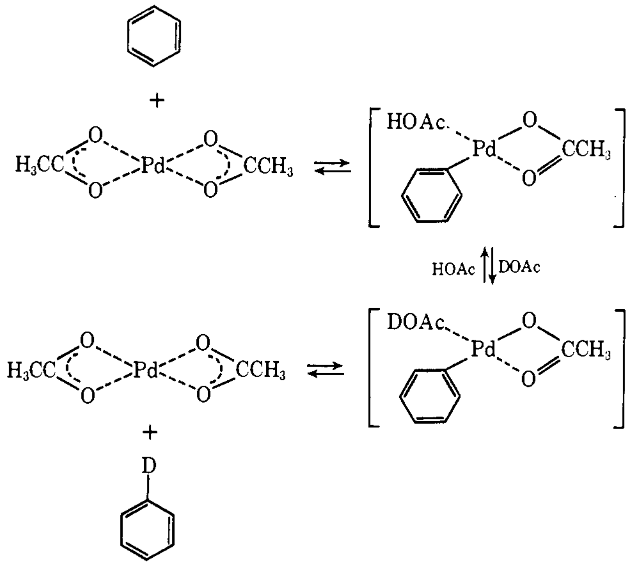
Isotope Effects in the Arylation of Olefins with Palladium(II) Acetate. The Mechanism of Olefin Arylation

Sir:

The mechanism of olefin arylation by palladium(II) compounds is quite complicated and is not well understood in spite of significant work in the area.[1-3] It is generally agreed that a σ-bonded palladium–aryl species is involved and support for this belief exists in the literature.[4,5] Moritani and coworkers have found that benzene substituents affect the orientation, but not the overall rate, of coupling.[6] They interpret this to mean that, while a σ-bonded aryl–palladium complex is probably involved, formation of the aryl–palladium σ bond is not the rate-determining step of the reaction.

In work bearing on this, we have found that the phenylation of styrene with benzene and benzene-d_6 exhibits a significant kinetic isotope effect. In a competitive experiment[7] involving styrene (0.096 mol), benzene (0.119 mol), benzene-d_6 (0.119 mol), and palladium(II) acetate (0.002 mol) at 80° for 6 hr, stilbene is produced in which stilbene-d_0/stilbene-d_5 is 5.3 ± 0.1 by mass spectrometry. By the independent method[7] of kinetic isotope effect determination, we have found that reactions of benzene and benzene-d_6 with styrene and palladium(II) acetate give K_H/K_D = 5.0 ± 0.4.[8] Although a complex reaction may show an isotope effect either if the bond to the labeled atom is broken in the rate-determining step or if it is broken in a rapid reversible equilibrium preceding the rate-determining step, the latter possibility is unlikely in this case since no isotopic scrambling was observed in our competitive experiment.[9] Only benzene-d_0 and benzene-d_6 were present in the final reaction mixture instead of the mixture of isomers to be expected if an equilibrium, such as that shown below, were operating. Thus, our data indicate that palladium–aryl σ-bond formation is a slow, irreversible step in olefin arylation.





A mechanism involving palladium–olefin σ-bond formation as the rate-determining step has been postulated for this reaction.[10] If this is correct, styrene-β,β-d_2

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[1] I. Moritani, S. Danno, Y. Fujiwara, and S. Teranishi, *Bull. Chem. Soc. Jap.*, 44, 578 (1971), and prior papers of this series.

[2] R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968).

[3] R. F. Heck, *ibid.*, 91, 6707 (1969).

[4] J. M. Davidson and C. Triggs, *J. Chem. Soc. A*, 1324, 1381 (1968).

[5] J. Tsuji, *Accounts Chem. Res.*, 2, 144 (1969).

[6] Y. Fujiwara, I. Moritani, R. Asano, H. Tanaka, and S. Teranishi, *Tetrahedron*, **25**, 4815 (1969).

[7] L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., pp 103–105.

[8] Since the independent method gives the isotope effect on the overall rate-determining step of the reaction (or a weighted mean if subsequent steps have comparable rates) while the competitive method gives the isotope effect on that particular step in the reaction which discriminates between the isotopically different species, the two methods need not necessarily give the same value for K_H/K_D.[7]

[9] Also, an isotope effect of this magnitude would not generally be expected to arise from a bond to the labeled atom being broken in an equilibrium step preceding the rate-determining step of the reaction.

[10] S. Danno, I. Moritani, and Y. Fujiwara, *Tetrahedron*, **25**, 4819 (1969).