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 $C_7H_8^+$.

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),

(1) I. Moritani, S. Danno, Y. Fujiwara, and S. Teranishi, *Bull. Chem. Soc. Jap.*, **44**, 578 (1971), and prior papers of this series.
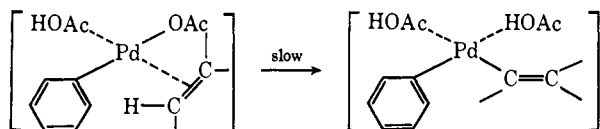
(2) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968).

(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).

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]
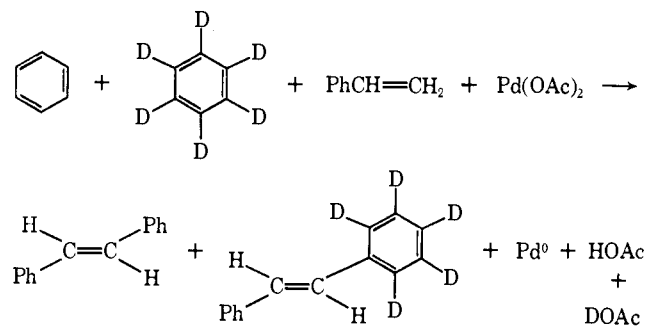
of kinetic isotope effect determination, we have found that reactions of benzene and benzene-d_6 with styrene and palladium(II) acetate give $K_H/K_D = 5.0 ± 0.4$.[8] Although a complex reaction may show an isotope effect either if the bond to the labeled atom is broken in the rate-determining step or 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
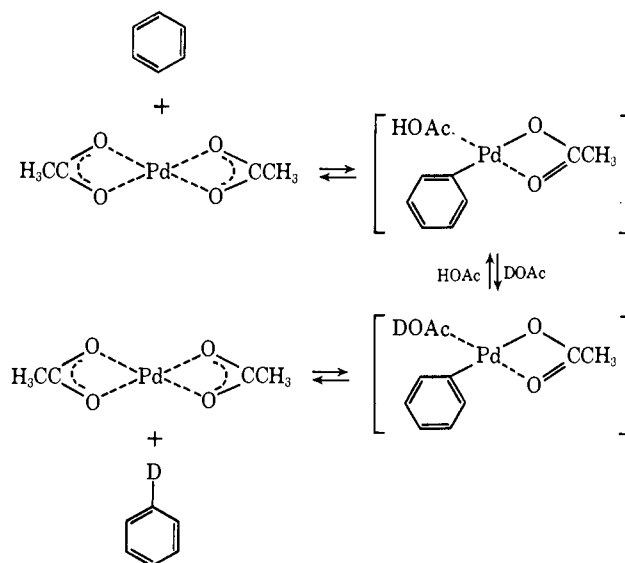
indicate that palladium–aryl σ-bond formation is a slow, irreversible step in olefin arylation.

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

(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).

should exhibit a primary kinetic isotope effect when coupled with benzene.[11] We have carried out the palladium(II) acetate effected coupling of benzene with styrene and styrene-β,β-d_2 under both competitive and independent conditions and have found only a small isotope effect. The independent reactions give $K_H/K_D = 1.25 \pm 0.08$. Precise interpretation of mass spectrometry data of a competitive run is complicated by the presence of a small amount of styrene-β-d_1 in the starting material, but a value of $K_H/K_D \approx 1$ is indicated. While rare examples of reactions presumably involving C–H bond cleavage in their rate-determining steps are known which exhibit kinetic isotope effects of less than 2,[13] primary kinetic hydrogen isotope effects are generally in the range of 2–9. A value as low as that observed here is indicative of a secondary isotope effect and suggests that cleavage of the styrene-β-hydrogen bond is not involved in the rate-determining step of olefin arylation.

Acknowledgment. The assistance of J. A. Favre with mass spectrum measurements and interpretations is gratefully acknowledged.

(11) Moritani and coworkers have recently reported the reaction between benzene, styrene-β,β-d_2, and palladium(II) acetate, [2] but their concern was with establishing the absence of a hydride shift in the mechanism rather than in determining an isotope effect.

(12) S. Danno, I. Moritani, and Y. Fujiwara, *Chem. Commun.*, 610 (1970).

(13) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961), and references therein.

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Limitations of the Use of Conformational Energies of Substituents in Bicyclo[2.2.1]heptane[1,2]

Sir:

The determination of the conformational energies of substituents attached to cyclohexane has been a central goal of conformational analysis for many years.[3,4] For most substituents, the values have been determined by a variety of techniques both direct and indirect, by physical and chemical methods and in a number of phases over a considerable range of temperatures. In light of the effort expended in obtaining conformational energies, it would be useful if these quantities could be utilized in at least a qualitative manner in other ring systems. In this report, the applicability of conformational energies in the widely studied bicyclo[2.2.1]heptane system is examined for the substituents methyl, hydroxyl, carbomethoxy, and nitro.

(1) Part XVI in a series entitled Conformational Analysis. Conformational Analysis. XV: R. J. Ouellette, D. Baron, J. Stolfo, A. Rosenblum, and P. Weber, *Tetrahedron*, submitted for publication.

(2) This research was supported by Grant No. GP-9231 from the National Science Foundation.

(3) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, pp 36–128, 436–442.

(4) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

2-Methylbicyclo[2.2.1]heptane was equilibrated directly at 300° over a Pd/C catalyst in a sealed tube. The calculated ΔG value given in Table I represents the

Table I. Comparison of Conformational Energies (Kilocalories per Mole)

Group	Cyclohexane	Bicyclo-[2.2.1]heptane	T, °C
CH_3	1.70	0.89	300
OH	0.95	1.05	82
CO_2CH_3	1.27	0.65	75
NO_2	1.20	1.38	100

stability of the exo over the endo isomer. For comparison, the conformational energy of methyl on cyclohexane is also given. An equilibration in the 200–300° range yields the most directly comparable value.[5] However, the value of 1.70 kcal/mol is one of the best established quantities and is apparently essentially an enthalpy dominated term.[4] Using the methyl group as a reference substituent, the generalization could be made that the conformational energies in bicyclo[2.2.1]-heptane are approximately one-half those of cyclohexane. However, equilibration of bicyclo[2.2.1]heptan-2-ol using Raney nickel in refluxing isopropyl alcohol yields a free-energy difference of 1.05 kcal/mol[6,7] which is larger than that of the methyl group. A direct comparison with the value for the cyclohexane ring determined by Eliel[8] under the same conditions is given in Table I. In the case of hydroxyl, the conformational energy is larger in bicyclo[2.2.1]heptane than in cyclohexane.

A comparison of the trigonal groups carbomethoxy and nitro in both cyclohexane and bicyclo[2.2.1]heptane is given in Table I. The values in bicyclo[2.2.1]heptane were determined using methanol and sodium methoxide for the carbomethoxy group and *tert*-butyl alcohol and potassium *tert*-butoxide for the nitro group. These conditions are the same for the cyclohexane compounds.[9–11] If carbomethoxy were used as a reference substituent for the two ring systems, the generalization could again be made that conformational energies of bicyclo[2.2.1]heptane are one-half those of cyclohexane. However, the nitro group is clearly larger than expected in bicyclo[2.2.1]heptane.

A rationale for the larger than expected conformational energies of hydroxyl and nitro in bicyclo[2.2.1]-heptane when compared to methyl and carbomethoxy must involve detailed force-field calculations. Qualitatively an argument based on bond lengths and steric environments of the axial position of cyclohexane compared to the endo position of bicyclo[2.2.1]heptane provides some insight. The shape of the potential

(5) Unpublished results of W. Szkrybalo, F. A. Van Catledge, and N. L. Allinger cited in ref 4.

(6) This value is in good agreement with one of 1.03 kcal/mol calculated by these authors from the data of Wilcox[7] obtained at 100° using aluminum isopropoxide.

(7) C. T. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

(8) E. L. Eliel and E. C. Gilbert, *J. Amer. Chem. Soc.*, **91**, 5487 (1969).

(9) R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, **31**, 587 (1966).

(10) The value for carbomethoxy is in good agreement with that of 1.29 kcal/mol calculated from the thermodynamic parameters of Eliel.[11]

(11) E. L. Eliel and M. C. Rees, *J. Amer. Chem. Soc.*, **90**, 1560 (1968).