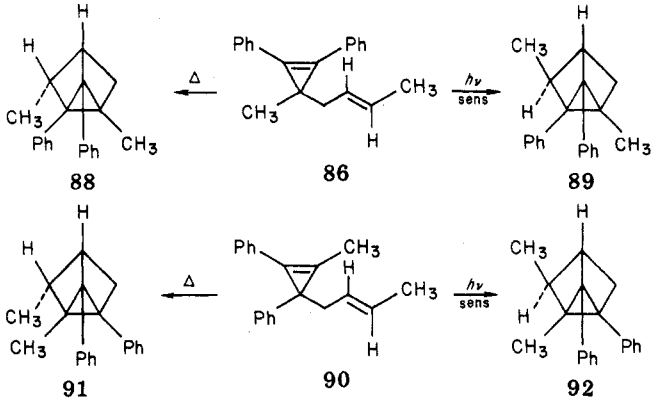
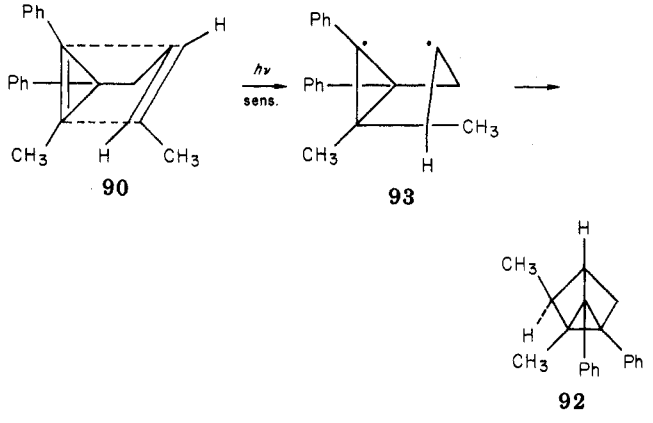
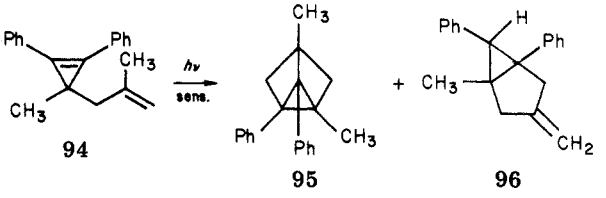


let-induced 2 + 2 cycloaddition reactions of these allyl-substituted cyclopropenes. It is tempting to suggest that the triplet-induced cycloaddition reactions of these systems proceed through a six-center, boatlike conformation. The secondary overlap of the frontier orbitals involved in the 2 + 2 cycloaddition reaction should favor the boatlike arrangement in the excited state and disfavor it in the ground state.



That these triplet-induced cycloaddition reactions are not concerted processes was demonstrated by the finding that cyclopropene **94** gave rise to a 2 + 2 adduct (**95**) and a bicyclohexane (**96**) on triplet sensitization.



The formation of **96** proceeds via an intramolecular hydrogen-transfer reaction. Both products were equally quenched with added triplet quenchers, thereby indicating that they are both derived from a common triplet state.

Conclusion

Cyclopropene derivatives have been found to undergo a wide array of novel photochemistry. The photobehavior encountered is markedly dependent on the substituent groups present and the multiplicity of the excited state. Significant progress has been made toward understanding the factors which determine the photochemical behavior in a given system. Further work will be needed to clarify the mechanistic features of some of the systems.

It is a pleasure to acknowledge the vital contribution of my collaborators, whose names are to be found in the references. Our studies have been generously supported by the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund, administered by the American Chemical Society.

Inductive Enhancement of Neighboring Group Participation

JOSEPH B. LAMBERT,* H. WAYNE MARK, ALLEN G. HOLCOMB, and ELAINE STEDMAN MAGYAR

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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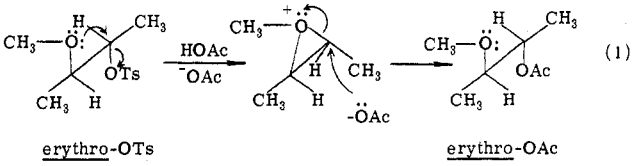
The nucleophilic displacement reaction (S_N) is particularly rapid when the nucleophile and the leaving group are in the same molecule 1). Such intramolecular



(1)

displacement, which has been termed anchimeric assistance or neighboring group participation, occurs not only in appropriate organic systems but also in many biochemical processes. Among the internal nucleophiles believed to be able to carry out such displacements are those possessing nonbonding electrons (halogen, oxygen, nitrogen, sulfur), those containing a π bond (double and

Joseph B. Lambert was born in Illinois and educated in Texas (elementary through high school), Connecticut (B.S., Yale, 1962), and California (Ph.D., Caltech, 1965). Since 1965, he has been on the staff at Northwestern University, where he is Professor of Chemistry. He has carried out research in the areas of conformational analysis, nuclear magnetic resonance, organic reaction mechanisms, and archaeological chemistry. The last area developed from a Guggenheim Fellowship at the British Museum Research Laboratory in 1973.

H. Wayne Mark, Allen G. Holcomb, and Elaine Stedman Magyar received their Ph.D. degrees at Northwestern in recent years. Mark has been on the staff of the Philips Research Center of Philips Petroleum Company since 1975. Holcomb has been on the staff of the 3M Company since 1974. Magyar has been Assistant Professor of Chemistry at Rhode Island College since 1978.

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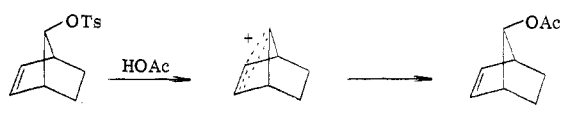
triple bonds, allenes, aryl groups), and those with the ever controversial single bond.[1,2]

Participation of the n, π, or σ electrons creates a full or partial bond to the site at which the leaving group has resided. Thus in eq 1, methoxy displaces tosyloxy to form an oxirane intermediate. Solvent reopens the ring by nucleophilic displacement on the C–O bond to form the product. Each of these steps occurs with inversion, and the net effect of two inversions is retention in eq 1 (*erythro*-OTs → *erythro*-OAc). Direct S_N2 displacement by solvent would have given a net inversion (*erythro*-OTs → *threo*-OAc), and a unimolecular loss of tosylate to give a carbonium ion without neighboring group participation would have given a mixture (*erythro*-OTs → *erythro*-OAc + *threo*-OAc).

The two most frequently employed tests for neighboring group participation have been rate enhancement and retained stereochemistry. The rate is increased because of the greater likelihood of intramolecular displacement. The stereochemical test is most relevant for those cases in which the product structure is the same as the starting material structure, except for replacement of the leaving group by the external (usually solvent) nucleophile, as in eq 1. Because starting material and product do not always have the same carbon framework, and because stereochemical arguments can involve considerable subtleties, the nonspecialist has tended to accept rate enhancements as a more convincing criterion for the demonstration of internal participation. Thus the 10^{11} rate enhancement[3] of *anti*-7-norborn-2-enyl tosylate (1)



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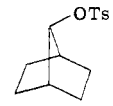

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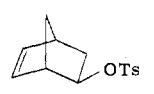
compared to that of its saturated counterpart **2** convinced many chemists that π bond anchimeric assistance exists. The fact that the product was formed with retention provided stereochemical confirmation.

Unfortunately, all too often even in seemingly favorable cases, significant rate enhancements simply are not observed, or their interpretation is subject to equivocation because a good nonparticipating model system is not available. Placement of the leaving group in a different position in the norbornenyl framework, as in **3**, actually results in a rate retardation in com-



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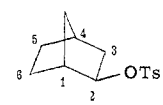

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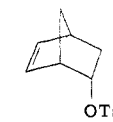

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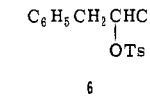
parison with its saturated analogue **4** (k_{unsat}/k_{sat} = 0.3 for acetolysis at 75 °C).[4] Apparently the stereoelectronic relationship between the double bond and the leaving group in **3** is much less favorable than that in **1**, and the electron-withdrawing polarity of the double bond acts as a rate retardant. An alternative kinetic comparison can be made between the exo compound **3** and its endo analogue **5**, in which the double bond is improperly directed for internal backside displacement on the leaving group. The k_{exo}/k_{endo} (**3**/**5**) ratio here is about 400 for acetolysis at 100 °C. Although at first glance this ratio might be thought to indicate a rate enhancement, nothing at all can be said without an accurate assessment of the normal differences between exo and endo reactivity. From the single observation of k_{unsat}/k_{sat} (0.3), there certainly is no demanding kinetic evidence for double bond participation, unless a particularly large inductive effect of the double bond can be invoked.

Participation by the π electrons of aryl groups provides another example of a rate deceleration despite reasonable stereochemical evidence for aryl anchimeric assistance.[5] Thus 1-phenyl-2-propyl tosylate (**6**)



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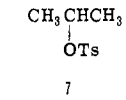

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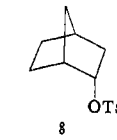

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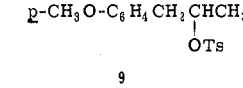
acetolyzes 0.32 as fast as the saturated 2-propyl tosylate (**7**) at 100 °C. Dissection of the overall rate into aryl participation and solvent participation in fact demonstrates that anchimeric assistance is important.[6]

Finally, mention must be made of *exo*-2-norbornyl tosylate (**4**), which some consider one of the most interesting molecules in organic chemistry, and others the most overstudied. Participation by the 6,1 single bond is stereoelectronically possible in the exo form, but impossible in the endo form **8**. The rate ratio (k_{exo}/k_{endo}) of 280 for acetolysis at 25 °C[7] again is subject to equivocation without a good measure of normal exo/endo differences.

Since a number of seemingly good candidates for anchimeric assistance (**3**, **6**, **4**) either exhibit rate retardations as measured by k_{unsat}/k_{sat} or provide equivocal rate enhancements as measured by k_{exo}/k_{endo}, we sought a new procedure for enhancing and discerning anchimeric assistance in these ambiguous cases.

Electronic Manipulation of Neighboring Group Participation

Placement of substituents directly on a participating entity can radically alter its ability to serve as an intramolecular nucleophile. Thus in aryl participation, the *p*-anisyl group (**9**) participates more strongly than



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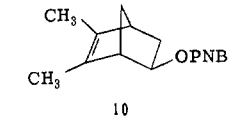

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the phenyl group in **6**,[6] and in double bond participation, a propenyl or a 2-butenyl group (**10**) participates more strongly than the ethenyl group in **3**.[8] In both

(1) B. Capon and S. P. McManus, "Neighboring Group Participation", Plenum Press, New York, 1976.
(2) H. C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York, 1977.
(3) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).
(4) J. B. Lambert and A. G. Holcomb, *J. Am. Chem. Soc.*, **93**, 2994 (1971).
(5) J. A. Thompson and D. J. Cram, *J. Am. Chem. Soc.*, **91**, 1778 (1969).
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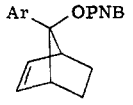
cases, the participating entity is more strongly electron donating, and hence is better able to participate. Alteration of the participating entity through substitution, however, answers no questions about the parent, unsubstituted functionality. Evidence that *p*-anisyl or 2-butenyl participates strongly does not give direct information on phenyl or ethenyl. It would be useful to have a method whereby participation of these unsubstituted functionalities could be manipulated.

Gassman and co-workers[9,10] in a seminal piece of work pointed the way for much of the future activity in this area. They observed that placement of an aryl group at the syn-7 position of the *anti*-7-norborn-2-enyl system (**11**) nearly quenches the strong double bond



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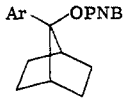

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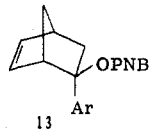
participation that had been observed in **1**. The k_{unsat}/k_{sat} that was 10^{11} for **1/2** is reduced to 3 for **11/12** with Ar = *p*-$CH_3OC_6H_4$, 41 for Ar = C_6H_5, or 35 000 for Ar = *p*-$CF_3C_6H_4$. For the *p*-anisyl case, the product in fact is a mixture of retention and inversion. In a qualitative sense, the developing carbonium ion is sufficiently stabilized benzylically that neighboring group participation becomes less necessary. Quantitative examination of the rate ratios shows that participation is a linear function of the electron demand at the site of positive charge development.

The term electron demand refers to the electronic requirements of a given electrophilic site. An unstabilized carbonium ion would have very high electron demand, and increased stabilization would diminish this demand. If electron demand is very low, as for the *p*-anisyl-substituted case (CH_3O donates electrons strongly), the double bond at the 2 position offers little or no kinetic participation. When the aryl group is absent, as in the parent **1**, electron demand is high, and participation is very strong.

Gassman and Fentiman[10] also noted that the ρ^+ value for these solvolyses is much lower (−2.30 at 25 °C for **11**) than for the aryl-substituted systems that are incapable of double bond participation (−5.17 at 25 °C for **12**; typically −4 to −6 for *tert*-cumyl cations). The Hammett slope is altered because double bond participation begins taking over as the primary mode of carbonium ion stabilization at the extreme of strongly electron-withdrawing aryl groups (increased electron demand).

Brown and co-workers utilized the Gassman–Fentiman approach as a test for the presence of participation. Comparison of the Hammett slope for a series of aryl-substituted systems capable of some form of participation or conjugation with that of corresponding systems incapable of such participation (exo vs. endo, unsaturated vs. saturated) provided a test for the existence of neighboring group participation. They applied the test to numerous systems, including 2-aryl-2-norbornenyl (**13**),[11] 2-aryl-5-methyl-2-norbornenyl



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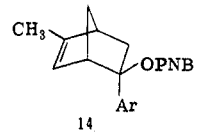

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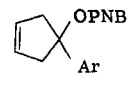

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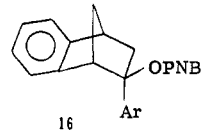

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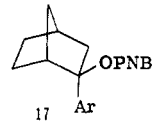

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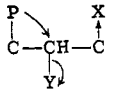
(**14**),[12] 1-arylcyclopent-3-enyl (**15**),[13] 2-aryl-2-benzonorbornenyl (**16**),[14] and 2-arylnorbornyl (**17**).[15] The ρ^+ values were interpreted in terms of the degree of participation, by comparison with that in the nonparticipating control system (the endo-OPNB isomer for **13**, **14**, **16**, and **17**; the saturated system for **15**).

One drawback to all these systems is that the parent system, e.g., **3** or **4**, is secondary, whereas the test series, e.g., **13** or **17**, is tertiary. Even the most electron-withdrawing aryl groups (such as 3,5-bis(trifluoromethyl)phenyl) do not attain the electron demand of the parent secondary system. Consequently, the entire tertiary series must exhibit less participation than the secondary compound. In the present studies, it was our objective to produce secondary systems that contain the functionalities of borderline participating ability and that have even higher electron demand than the parent. An increase in the electron demand should bring about greater neighboring group participation, as discerned by clear-cut rate enhancements. We have taken this approach for three modes of participation, double bond (homoallylic), aryl, and single bond, and this Account describes the results of these experiments.

Enhancement of Double Bond Participation

Electron demand can be manipulated by substitution at remote positions as well as by substitution directly on the carbon atom attached to the leaving group. Whereas direct substitution by definition must convert the ion to tertiary, more remote substitution maintains it secondary. The strongest perturbation naturally will be felt by substitution at the nearest neighbor carbons. Structure **18** illustrates the requirements for bringing



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about increased electron demand by such substitution. The group P must be sterically and electronically capable of participation, Y must be an appropriate leaving group, and X must be a strongly electron-withdrawing group. Throughout this study, the leaving group Y is always tosylate (OTs). The perturbing substituent X must be incapable itself of participating, for either steric or electronic reasons.

In our initial studies,[4] the participating entity P was a double bond, incorporated into either the bicycloheptene or the bicyclooctene structure. Compound **19** possesses all the relevant features of **18**. The second tosyloxy group, located at the 3 position, is the per-

(8) P. G. Gassman and D. S. Patton, *J. Am. Chem. Soc.*, **91**, 2160 (1969).
(9) P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968).
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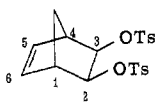
(13) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **97**, 7454 (1975).
(14) H. C. Brown, S. Ikegami, K.-T. Liu, and G. L. Tritle, *J. Am. Chem. Soc.*, **98**, 2531 (1976).
(15) H. C. Brown, M. Ravindranathan, K. Takeuchi, and E. N. Peters, *J. Am. Chem. Soc.*, **97**, 2899 (1975).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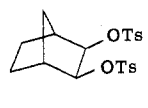
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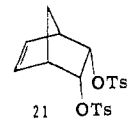
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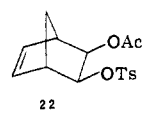
turbing entity. The departing tosylate is exo, since endo leaving groups experience no neighboring group assistance from a 5,6 double bond. Electron withdrawal by the second tosyloxy group increases electron demand at the 2 position, so that a greater amount of double bond participation is required. As positive charge develops at the 2 position, double bond participation moves the charge further from the remaining tosyloxy group.

We may use the same kinetic criteria mentioned in the monotosylate series above. The first-order rate for **19** is compared to that of similar systems in which double bond participation is impossible. The saturated ditosylate **20** provides one such comparison. The ratio k_{unsat}/k_{sat} (**19**/**20**) was observed[4] to be 506 for acetolysis at 75 °C. This figure represents a substantial rate enhancement. Compared to the analogous rate ratio in the monotosylate series (0.30), the total kinetic enhancement of participation is about 1700 (506/0.3). To be sure, the ditosylates acetolyze at a much slower overall rate than the monotosylates because of the electron-withdrawing effect of the second tosylate group. Participation, however, is measured not from the absolute rates but from the relative rates of participating and nonparticipating species. In fact, it is this lower overall rate that brings out the enhanced participation.

Another valid comparison would be between the di-exo ditosylate **19** and its di-endo analogue **21**. Here k_{exo}/k_{endo} (**19**/**21**) is observed to be about 140 000 for acetolysis at 25 °C,[4] compared to about 4000 for the monotosylate series (**3**/**5**). Thus by either the k_{unsat}/k_{sat} or the k_{exo}/k_{endo} criterion, the ditosylate exhibits much stronger double bond participation than the monotosylate. The use of rate ratios always means that ditosylate rates are being divided by ditosylate rates and monotosylate rates by monotosylate rates. Thus the statistical factor associated with one vs. two possible leaving groups is avoided.

Another procedure for achieving enhanced participation is to use a perturbing substituent (X in **18**) that is incapable of being a leaving group under our conditions. For this reason we prepared the acetoxy tosylates **22** and **23**. The k_{unsat}/k_{sat} here is about 50 for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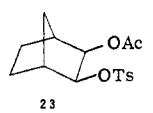
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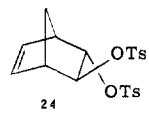

24

acetolysis at 75 °C,[4] again substantially larger than that in the monotosylates. The enhancement of double bond participation is smaller in **22** than in **19** because acetoxyl is less electron withdrawing than tosyloxyl. It is important to note that the syn dihedral relationship between the acetoxy and the tosyloxy groups in **22** prohibits acetoxy participation.

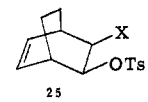
Another useful control compound is the trans ditosylate **24**. The endo tosyloxy group cannot serve as the first leaving group (Y in **18**), since it is incapable of experiencing double bond participation. Nonetheless, it can still serve as the perturbing element (X). In fact, the di-exo (**19**) and the trans (**24**) compounds have essentially the same acetolysis rates (**19**/**24** = 1.08 at 75 °C). Two conclusions may be drawn from this observation. First, an endo tosyloxy group is as effective at enhancing double bond participation as an exo tosyloxy group. Therefore, the mode of electron demand manipulation is probably inductive (through bond) rather than field (through space). Consequently, we refer to the general phenomenon as "inductive enhancement of neighboring group participation". Second, the equivalence of the cis and trans rates eliminates the possibility that the two exo tosylate groups depart simultaneously to form a bishomocyclobutenium dication,[16] since the endo tosylate group in **24** would depart much more slowly than the exo group.

The overall mechanism is shown in eq 2 (X can be


(2)

OAc or OTs, exo or endo), in which the rate-determining step is departure of the exo tosylate with double bond participation to form a homoallylic or cyclopropylcarbinyl intermediate, which can produce all the observed products.[4]

Enhancement of double bond participation can also be effected in the bicyclooctene series.[17] The monotosylate k_{unsat}/k_{sat} is somewhat larger [(**25**, X = H)/(**26**, X = H) = 63 for acetolysis at 75 °C] than in the bi-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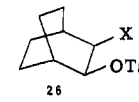
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cycloheptene series (**3**/**4** = 0.3). The octene molecule is not so rigid as the heptene, so that the double bond in **25** (X = H) must be slightly better situated for participation than that in **3**. In the ditosylate octene series, the k_{unsat}/k_{sat} [(**25**, X = OTs)/(**26**, X = OTs)] is 6850, one of the largest double bond rate enhancements observed outside of symmetrical bishomocyclopropenium structures. The enhancement of double bond participation is the ratio of these two figures, 6850/63 = 110. It appears that the net enhancement of participation is less (110) in the octene series than in the heptene series (1700). For the heptene, there is very little double bond participation in the monotosylate, so there is greater need for delocalization in the ditosylate. In the octene, there is substantial participation already in the monotosylate, so less additional participation is needed in the ditosylate.

In this double bond series, we have seen that introduction of an adjacent electron-withdrawing group enhances participation in the departure of the leaving group. The degree of magnification depends on the electron-withdrawing ability of the perturbing group, e.g., OAc vs. OTs, and on the amount of already existing participation, e.g., bicycloheptene vs. bicyclooctene. The procedure has been able to magnify participation, so that weak or nonexistent double bond participation in the monotosylate **3** is clearly manifested in the ditosylate **19**.

(16) J. B. Lambert and A. G. Holcomb, *J. Am. Chem. Soc.*, **91**, 1572 (1969).

(17) J. B. Lambert and A. G. Holcomb, *J. Am. Chem. Soc.*, **93**, 3952 (1971).

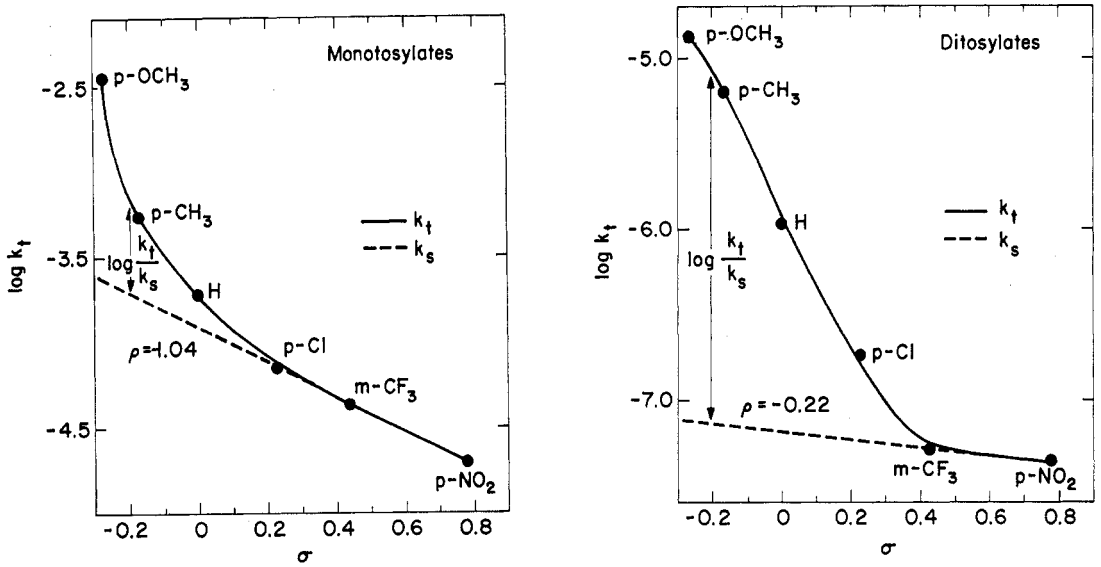


Figure 1. (Left) The overall acetolysis rate (k_t, solid line) for 1,4-diaryl-2-butyl tosylates (**28**) as a function of the Hammett σ constant. (Right) The overall acetolysis rate for *meso*-1,4-diaryl-2,3-butyl ditosylates (**27**). The dotted line in both plots represents the solvent participation component (k_s) of the reaction.

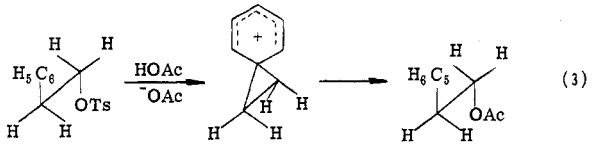
Table I
Percentage of Aryl Participation ($100Fk_\Delta/k_t$)

substituent	monotosylate (**28**)	ditosylate (**27**)
p-OCH_3	93	99
p-CH_3	66	99
H	35	94
p-Cl	0	68
m-CF_3	0	0
p-NO_2	0	0

[a] Remaining percentage is solvent participation (k_s).

Enhancement of Aryl Participation

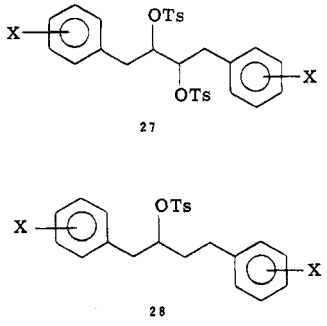
Like unsymmetrical double bond participation, aryl participation (eq 3) appears to be kinetically very weak,



(3)

aryl groups even causing rate retardations.[6] The problem lies in the difficulty of separating what may be strong neighboring group participation (k_Δ) from similarly strong solvent participation (k_s).[6,18] Simple ionization (k_C) cannot compete with either of these processes in a strongly nucleophilic medium. The titrimetric (overall) rate (k_t) may be resolved into its two components by a Hammett procedure, so that k_Δ alone may be examined. A Hammett plot (log k_t vs. σ) is constructed by varying the substitution on the aryl ring and hence its neighboring group ability. The aryl ring with strongly electron-withdrawing (poorly participating) groups solvolyzes only by solvent assistance ($k_t = k_s$). Those points form a typical Hammett plot for direct nucleophilic substitution (S_N2) and can be extrapolated to give k_s for the other substituents. Deviations of k_t from this line give a direct measure of neighboring group participation ($Fk_\Delta/k_t = 1 - k_s/k_t$) ($F$ is the fraction of bridged arylonium ion that goes on to product).

To test whether the procedure of inductive enhancement of participation can be applied to aryl participation, we needed to prepare a system of the general structure **18** in which the participating entity P is phenyl. We settled on the series **27**, *meso*-1,4-diaryl-2,3-butyl ditosylate, for observation of enhanced aryl participation, with **28** as the control for normal aryl participation.[19] These materials could be conveniently prepared from the *cis*-1,4-diaryl-2-butenes respectively by hydroxylation and hydration.[19] In this series, one tosyloxy group serves as the leaving group Y and the other as the inductively perturbing group X. The second aryl group is necessary in **27** in order to render the two tosyloxy groups equivalent. The rate-determining step should be departure of the first tosylate group, either by aryl assistance or by solvent displacement (acetic acid). Tosyloxy assistance as usual should be negligible. Because this series is open chain, acetoxy could not be used as the perturbing group X, as acetoxy participation to form an acetoxonium ion would probably predominate. In fact, we found that the acetoxy tosylate solvolyzed much more rapidly than did the corresponding ditosylate **27**.



X
a p-OCH_3
b p-CH_3
c H
d p-Cl
e m-CF_3
f p-NO_2

The Hammett plots for dissection of the overall rate k_t into its k_Δ and k_s components, as described above, are given in Figure 1. It can be seen immediately that

(18) C. J. Kim and H. C. Brown, *J. Am. Chem. Soc.*, **91**, 4287, 4289 (1969); C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4291, 4296 (1969); C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *ibid.*, **91**, 4296 (1969); H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970); H. C. Brown and C. J. Kim, *ibid.*, **93**, 5765 (1971).

(19) J. B. Lambert, H. W. Mark, and E. Stedman Magyar, *J. Am. Chem. Soc.*, **99**, 3059 (1977).

the deviations of k_t (solid line) from k_s (dotted line) are much more dramatic for the ditosylate (Figure 1, right) than for the monotosylate (Figure 1, left). Table I contains the percentages of aryl participation calculated from these deviations. The figures in the middle column for our monotosylate **28** are very similar to those obtained by Schleyer and by Brown[18] for 2-butyl and 2-propyl tosylates. Consequently, the extra phenyl group that was present because of the mode of synthesis must be entirely nonfunctional in this context. The nitro, trifluoromethyl, and chloro substituents define the k_s line and hence exhibit no aryl participation. Phenyl itself shows more solvent assistance (65%) than aryl assistance (35%). *p*-Tolyl shows moderately strong aryl assistance (66%), and *p*-anisyl is quite strong (93%). Introduction of the second tosyloxy group slows the entire reaction considerably.[19] The nitro and trifluoromethyl groups define the k_s line, and all other substituents show deviations therefrom. The previously weak participator phenyl is now quite strong (94%). Both *p*-tolyl and *p*-anisyl show essentially all aryl participation (99%). Even *p*-chloro now shows aryl participation (67%).

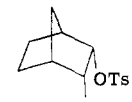
It appears that introduction of an electron-withdrawing group on the carbon adjacent to the reactive site indeed enhances aryl participation. Removal of electron density by the β-tosyloxy group increases electron demand at the reactive site, thereby requiring greater aryl assistance. Delocalization of the positive charge into the aryl group places it at a greater distance from the remaining electron-withdrawing tosyloxy group than would be the case in the absence of aryl participation. These effects can be discussed in terms of relative rate enhancements as well as in percent k_Δ pathway. The value of k_t/k_s (the overall rate including aryl participation, divided by the rate of solvent assistance alone) increases from 1.55 for the phenyl monotosylate (**28c**) to 16.6 for its ditosylate (**27c**), an enhancement of 10.7. The corresponding figures for *p*-tolyl are 91.2/2.95 = 31, for *p*-anisyl are 182/15.5 = 11.7, and for *p*-chloro are 3.16/1.0 = 3.16. The observed products are entirely in accord with these observations but cannot give independent confirming evidence.[19]

In the aryl series, introduction of an adjacent electron-withdrawing group converts phenyl, *p*-tolyl, and *p*-anisyl from a mixture of solvent and aryl participation to essentially all aryl participation. Even *p*-chloro becomes a reasonably strong participator. Thus aryl groups do respond to increased electron demand at an adjacent site of developing positive charge by offering an increased level of participation. In these open-chain systems, any given diastereomer can assume the required anti stereochemistry between participator and leaving group by rotation about the C–C bond, in contrast to the norbornenyl system, in which diastereomers are structurally constrained. Nonetheless, to determine that there was no dependence on rotamer populations we also prepared the *dl* version of **27c** (phenyl) and found the same amount of enhancement of aryl participation as for the meso isomer.

Enhancement of σ Participation

A third proposed form of neighboring group participation that exhibits ambiguous kinetic enhancements involves σ bonds. The k_{exo}/k_{endo} rate ratios (**4**/**8**) between 10^2 and 10^3 were originally attributed to anchimeric assistance in the exo form.[20] The observation that equally large values of k_{exo}/k_{endo} are present in tertiary systems such as **17** with strongly electron-donating aryl groups[15] diminishes the value of this argument, since the decreased electron demand at the well-stabilized tertiary center would have much less need for participation. Although k_{exo}/k_{endo} rate ratios around 300, as found for the secondary systems (**4**/**8**) and for the tertiary systems **17**, cannot be the sufficient indicator of σ bond participation, it is possible that larger values might indicate such a phenomenon in systems with higher electron demand at the 2 position. Consequently, we applied our method of inductive enhancement of participation to the saturated norbornyl system to see whether kinetic evidence for σ participation could be adduced.[21]

Since σ participation should only be possible in an exo tosylate, compounds **20** (cis exo ditosylate) and **23** (cis exo acetoxy tosylate) were the necessary focus of this study. They incorporate an exo leaving group Y (as in **18**) and a perturbing electron-withdrawing group X, either tosyloxy or acetoxy. The nonparticipating model systems would be the analogous cis endo molecules, **29** and **30**. The acetolysis di-exo/di-endo rate



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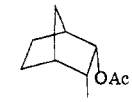

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ratios measured for these two pairs of compounds proved to be 50 for **20**/**29** (ditosylate) and 11 for **23**/**30** (acetoxy tosylate) at 25 °C, compared to about 300 for **4**/**8** (monotosylate).[7] Clearly, there has been no inductive enhancement of σ participation, which would have been indicated by an increased value of k_{exo}/k_{endo}. The ratio in fact has decreased.

Figure 2 provides a useful comparison between the results in the norbornyl series (**4**, **17**, **20**, **23**) and those with double bond participation in the closely related norbornenyl series (**3**, **13**, **19**). The ratio k_{exo}/k_{endo} is plotted as a function of electron demand measured by k_{endo}, the endo system now being considered a k_C (carbonium ion) system rather than solvent participation or neighboring group participation. The left-hand three points are for the variously substituted tertiary systems **13** and **17**, which provide decreased electron demand compared to the secondary system. The fourth point from the left in both plots is for the respective parent system, **3** and **4**. Finally, the rightmost points are the systems with adjacent electron-withdrawing groups, **19**, **20**, and **23**, which provide increased electron demand.

In the unsaturated series, the ratios for the tertiary systems of about 300 appear to represent the base line difference between exo and endo reactivity in the absence of participation. The value of 4000 for the secondary system **3**/**5** therefore is consistent with anchimeric acceleration of about a factor of 10. The secondary ditosylate ratio for **19**/**21** of 140 000 demonstrates the enhancement of double bond participation in the presence of increased electron demand. The plot for the saturated compounds is quite different. Here

(20) For a summary, see ref 2.
(21) (a) J. B. Lambert and H. W. Mark, *Tetrahedron Lett.*, 1765 (1976); (b) J. B. Lambert and H. W. Mark, *J. Am. Chem. Soc.*, **100**, 2501 (1978).

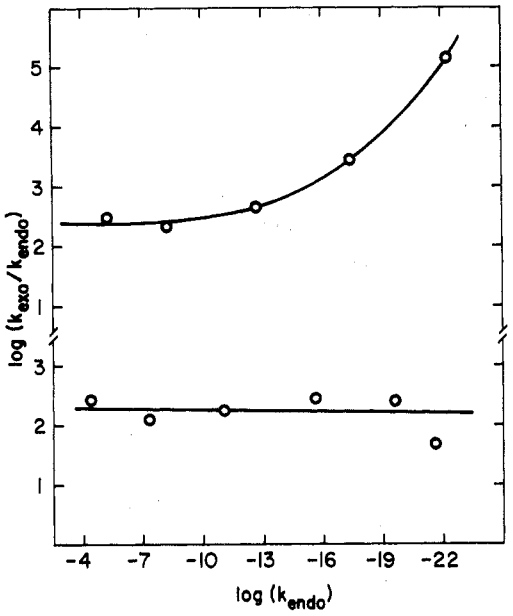


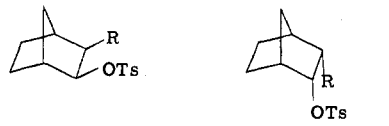
Figure 2. The exo/endo rate ratio for 2-norborn-5-enyl systems (upper curve) and for 2-norbornyl systems (lower curve) as a function of electron demand (k_{endo} adjusted to a common leaving group). The left three points in each curve are for tertiary systems, 2-aryl-2-norborn-5-enyl (*p*-methoxyphenyl, phenyl, and *m,m'*-bis(trifluoromethyl)phenyl) (**13**, **17**).[11,15] The fourth points from the left are for the parent secondary systems (**3**/**5**, **4**/**8**). The points on the right are for the inductively enhanced ditosylate (**19**/**21**, **20**/**29**) and acetoxy tosylate (**23**/**30**) systems. Reproduced from ref 21a with permission. Copyright 1976, Pergamon Press.

the tertiary compounds **17** and the secondary compound **4**/**8** have essentially the same ratio, close to 300. Again, this factor must represent the base line difference between exo and endo reactivity. In contrast to the unsaturated series, however, the increased electron demand provided by the ditosylate **20**/**29** or the acetoxy tosylate **23**/**30** brings about a smaller rather than a larger rate ratio.

The most straightforward conclusion to draw is that enhancement of participation was not observed in the σ systems because σ participation was entirely lacking in the first place. This would be a valid conclusion, provided that there is no fundamental difference between the saturated and unsaturated series. The most likely difference would be a steric effect on the saturated endo compounds **29** and **30**. Relief of steric interactions between the endo-2 leaving group and the endo-5,6 protons, not present in the unsaturated endo compound **21**, might provide an acceleration in k_{endo} for the saturated cases, **29** and **30**, in comparison to the unsaturated **21**. Such an endo acceleration might parallel an exo acceleration from enhanced σ participation in **20** and **23**, thereby nullifying any increase in the ratio k_{exo}/k_{endo}.

Examination of rate ratios in similar systems with even larger groups at the 3 position appears to exclude this argument. The k_{exo}/k_{endo} ratios can be computed from literature data for the phenyl and cyclohexyl compounds, 0.95 for **31**/**32** and 15 for **33**/**34**. These reduced ratios (reductions of about 300 and 20, respectively, from the ratio for the parent **4**/**8**) must be attributed to steric effects, since polar effects, particularly for cyclohexyl, must be very small.

Whereas the *A* value for cyclohexyl is about 2.5, the values for acetoxy and tosyloxy are 0.5–0.7. Consequently, the steric effect for the latter two substituents should be much smaller than the factor of 20 for the considerably larger cyclohexyl. It is quite possible that the observed reductions in k_{exo}/k_{endo} to 50 (a factor of 6) for tosyloxy and 11 (a factor of 30) for acetoxy are due in part to this steric effect. In light of the magnitude of the effect for cyclohexyl, however, it is unlikely that a large steric effect on k_{endo} could be obscuring a significant increase in k_{exo}/k_{endo} for acetoxy and tosyloxy. Even if the steric effect of these two substituents were half that of cyclohexyl (an unlikely event), the rate ratios corrected for the steric effect would increase respectively only to 110 and 500, still within about a factor of 2 of the base line for exo/endo reactivity (280).



31: R = C_6H_5 **32**: R = C_6H_5

33: R = C_6H_{12} **34**: R = C_6H_{12}

We find that electron demand far in excess of that in the parent norbornyl tosylate fails to elicit σ participation, at least as manifested in k_{exo}/k_{endo}. This conclusion, however, is subject to interpretation concerning the magnitude of the buttressing effect in the endo tosylate containing an endo electron-withdrawing group. Comparison with a 3-*endo*-cyclohexyl system, in which the steric effect should be much larger, suggests that the steric effect for the electron-withdrawing groups is not large enough to mask a palpable enhancement of σ participation.

Concluding Remarks

Introduction of an electron-withdrawing group such as tosyloxy or acetoxy on the carbon adjacent to the point of attachment of a leaving group can educe higher levels of neighboring group participation during solvolysis, in comparison to cases lacking such groups. Thus double bond participation is several orders of magnitude stronger kinetically in the ditosylate **19** and the acetoxy tosylate **22** than in the monotosylate **3**. Similarly, aryl participation is enhanced in the ditosylate **27**, in comparison to the monotosylate **28**, for most substituents. The enhancement is optimal for functionalities with moderate neighboring group abilities. Thus *p*-anisyl, which participates very strongly in the absence of the enhancing group, increases only a factor of 10 in the presence of the group. Apparently, if participation is already quite strong, enhancement is not maximal. In contrast, *p*-tolyl is enhanced about a factor of 30, the largest we observed in aryl participation. If the participating group is very weak, the enhancement becomes small. For *p*-chloro, the kinetic enhancement is only a factor of 3. In the extreme, negligibly participating entities cannot be turned into participating entities by this procedure. The plots in Figure 1 show this behavior very well. In Figure 1 (left) without enhancement, participation increases monotonically as the aryl group becomes more electron donating, so that the deviation of the solid line from the dotted line increases monotonically. In Figure 1 (right), the enhancement of participation begins to decrease with the most electron-donating substituents, so that the distance between the solid and dotted lines

is approaching a maximum.

In the final case we examined, the saturated 2-norbornyl tosylate **4**, it appears that σ participation by the 6,1 bond falls well below the threshold above which participation can be enhanced. Consequently, this procedure is limited to those cases in which participation is at or above the borderline for observability. Whereas we could bring out previously unobserved participation by *p*-chlorophenyl, we could not elicit any response from the σ bond. The procedure is further limited in each case (1) by the choice of models for the absence of participation and (2) by the choice of models for unenhanced participation, e.g., (1) **20** or **21** and (2) **3** for double bond participation in **19**. The method is also limited by the assumption that the introduction of the electron-withdrawing group X brings only an inductive effect. The problem of a possible steric effect in the σ bond series (**20**, **23**, **29**, **30**) had to be examined carefully.

With these limitations, the method of inductive enhancement of solvolytic participation should be applicable to a host of further modes of participation. There are a number of different cases involving participation by lone pairs, such as halogens, ethers, thioethers, amines, etc. Triple bond and cyclopropane participation could be examined as further representations of the π bond class. Whereas we have used only tosyloxy and acetoxy groups as the electron-withdrawing substituent, investigations could also include other functionalities such as cyano or trifluoromethyl.

Finally, it might be worthwhile to examine the effect of placement of the electron-withdrawing group X directly at the reactive site. The molecules of Gassman and of Brown (**11**–**17**) essentially served this purpose, but the electron demand achieved by the most electron-withdrawing aryl group at the α position was still less than that of tosyloxy or acetoxy at the β position in our systems. It would be worthwhile to examine the placement of much more strongly electron-withdrawing groups, such as trifluoromethyl, directly at the reactive site. These experiments are among the future directions studies might take in the general field of inductive enhancement of neighboring group participation.

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Catalytic Hydrogenation of Aromatic Hydrocarbons

EARL L. MUETTERTIES* and JOHN R. BLEEKE

Department of Chemistry, University of California, Berkeley, California 94720

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The art and science of metal and metal oxide catalyzed arene hydrogenations have been significantly advanced since Sabatier's original findings.[1] These catalytic hydrogenations are utilized in present-day technology,[2] but substantive issues and challenges remain. Mechanistically, the reactions are not fully defined.[3-5] In addition, none of these solid-state catalysts exhibits chemoselectivity or stereoselectivity features that could be of more general synthetic utility to the organic synthetic chemist. Chemoselectivity here refers to the rate of arene ring hydrogenation relative to other functional group hydrogenation rates. Stereoselectivity refers to the degree to which all six hydrogen atoms added to benzene or a benzene derivative in a hydrogenation appear on the same side of the resultant cyclohexane ring.

In 1973, we[6] accidentally discovered that a simple organocobalt molecule, η^3-$C_3H_5Co[P(OCH_3)_3]_3$,[7,8] was a solution-state catalyst for the hydrogenation of aromatic hydrocarbons. Reaction conditions were quite temperate—1 atm of hydrogen and room temperature. Most significantly, this catalyst was stereoselective[9-11] and, to a degree, chemoselective.[9-11] These findings

Earl L. Muetterties received his B.S. degree from Northwestern University and his Ph.D. degree from Harvard University (1952) working with C. A. Brown and E. G. Rochow. After an extended career at the Central Research Department of E. I. du Pont de Nemours and Company, he joined the chemistry faculty at Cornell University. He is now Professor of Chemistry at the University of California, Berkeley.

John R. Bleeke received his B.A. degree from Carthage College (1976) and his M.S. degree from Cornell University (1978). He is a National Science Foundation Predoctoral Fellow and is completing the requirements for the Ph.D. degree in the Department of Chemistry, University of California, Berkeley.

(1) Phenol and aniline were the first aromatic systems to be catalytically hydrogenated. These reactions were carried out in 1904 by Sabatier and Senderens, using nickel metal as catalyst. Cf. Sabatier, P.; Senderens, J. B. *Soc. Chim. Fr., Bull.* **1904**, [3] *31*, 101. The hydrogenation of benzene with a nickel catalyst was reported by Sabatier and Espil in 1914: Sabatier, P.; Espil, L. *Ibid.* **1914**, [4], *15*, 228.

(2) Rylander, P. N. "Catalytic Hydrogenation over Platinum Metals"; Academic Press: New York and London, 1967; Chapter 18. Weissermel, K.; Arpe, H-J. "Industrial Organic Chemistry"; Verlag Chemie: New York, 1978; p 301.

(3) Early mechanistic proposals were made by Horiuti and Polanyi and by Farkas and Farkas: Horiuti, I.; Polanyi, M. *Trans. Faraday Soc.* **1934**, *30*, 1164. Horiuti, I.; Ogden, G.; Polanyi, M. *Ibid.* **1934**, *30*, 663. Farkas, A.; Farkas, L. *Ibid.* **1937**, *33*, 678, 827.

(4) Crawford, E.; Kemball, C. *Trans. Faraday Soc.* **1962**, *58*, 2452; Harper, R. J.; Kemball, C. *Proc. Int. Congr. Catal., 3rd*, **1964**, *2*, 1145. Garnett, J. L.; Sollich, W. A. *J. Catal.* **1963**, *2*, 350.

(5) For a review of proposed mechanisms of heterogeneous hydrogenation see: Siegel, S. *Adv. Catal.* **1966**, *16*, 123.

(6) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 4063.

(7) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1973**, *95*, 5419; **1974**, *96*, 7920.

(8) Muetterties, E. L.; Hirsekorn, F. J. *J. Chem. Soc., Chem. Commun.* **1973**, 683.

(9) Rakowski, M. C.; Hirsekorn, F. J.; Stuhl, L. S.; Muetterties, E. L. *Inorg. Chem.* **1976**, *15*, 2379.

(10) (a) Stuhl, L. S.; DuBois, M. Rakowski; Hirsekorn, F. J.; Bleeke, J. R.; Stevens, A. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 2405. (b) Small amounts of other species were detected, but these were derived, in the experimental workup, from the decomposition of catalyst intermediates in which hydrogenation was incomplete. See discussion in ref 10a.

(11) Muetterties, E. L.; Rakowski, M. C.; Hirsekorn, F. J.; Larson, W. D.; Basus, V. J.; Anet, F. A. L. *J. Am. Chem. Soc.* **1975**, *97*, 1266.

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