Kinetic Studies of Reactions of Transition Metal Carbonyl Anion with Allyl Halides

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The reaction of $CpMo(CO)_3^-M^+$ ($M^+ = Li^+, Na^+, K^+, PPN^{+a}$) with allyl halide was performed and the details of its counterion effects and solvent effect was investigated under the pseudo-first order conditions. The kinetic data from this reaction were compared with those from the reaction of the same anion with benzyl halides in terms of their inverse counterion effects.

Introduction

For many years R. B. King's well-known relative nucleophilicity order of the transition metal carbonyl anions toward organic hilides[1] has been very valuable as a predictable guide for organometallic synthesis and possible intermediates in both stoichiometric and catalytic reactions. The displacement of X^- from RX by anionic metal carbonylates follows a second order rate law, rate $= k_2[M^-][RX]$.

$$M(CO)_x^- + RX \rightarrow X^- + RM(CO)_x \qquad (1)$$
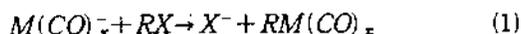
Many workers have studied the counterion effect on the structure and reactivity of the following carbonylates: $HFe(CO)_4^-$,[2] $Mn(CO)_5^-$,[3] $Co(CO)_4^-$,[4] $CpMo(CO)_3^-$,[5] and $CpW(CO)_3^-$.[6] For alkyl halides a "normal" counterion effect is observed; the less associated the anion is with its counterion, the greater is its nucleophilicity. However, an "inverse" counterion effect has been observed for reaction of $Co(CO)_4^-$, $Mn(CO)_5^-$, and $CpMo(CO)_3^-$ with the activated organic halides such as benzyl chloride or allyl chloride.[7] In such case, tight ion pairs were observed to enhance the reaction rate. This inverse counterion effect is more pronounced for weaker nucleophiles. This effect is most readily explained in terms of cation assistance of R-X bond cleavage where the RX molecule has some carbonium ion character or some charge separation.[5] In this paper, we would like to report the result of the kinetic studies on the reaction of $M^+CpMo(CO)_3^-$ ($M^+ = Li^+, Na^+, K^+, PPN^+$) with $CH_2 = CHCH_2X$ ($X = Cl, Br$) and the details of the reaction comparison between the above reaction and that of the corresponding anion with benzyl halides.

Experimental

An inert-atmosphere glove box and Schlenk line and/or high-vacuum techniques were employed for most of sample transfers and sample manipulations. Infrared spectra were recorded on either an IBM FTIR/32, IBM FTIR/85, or Perkin Elmer 283B spectrophotometer. Proton nuclear magnetic resonance spectra were obtained from either a 90 MHz Varian EM-339 or Varian XL200 MHz Spectrometer. Reaction temperature control was achieved with either Haake A81 or Precision R20 thermostat. Most of weighings and

transfers of compounds were carried out under an Ar atmosphere in the glove box (HE-63-P Vacuum Atmosphere Co.). Photoreactions were performed using a 450 watt Hg vapor lamp covering a rather broad range of UV-VIS wavelengths. Solvents were distilled under N_2 from appropriate drying and O_2 scavenging agents: tetrahydrofuran (THF) and toluene, $Na°/benzophenone$; hexane, $Na°/benzophenone/diglyme$; methylene chloride, P_2O_5; acetonitrile, CaH_2 followed by P_2O_5; ethanol, $Mg°/I_2$.[8] Common reagents were purchased from ordinary vendors and used as received without further purification. The organic halides were usually distilled from P_2O_5 and several freeze-pump-thaw degassings were applied prior to use.

Preparation of Anionic Transition Metal Carbonyl; ($CpMo(CO)_3^-$). The anionic metal carbonylates were usually prepared by reduction of the parent dimer[9] via Na/Hg amalgam according to the literature.[10,11] PPN^+ salts of each anion (~2 mmol) were prepared by mixing a 10 m*l* portion of THF containing the anion with a CH_2Cl_2 solution (about 4 m*l*) of an equivalent amount of PPN^+Cl^-. This solution was stirred and filtered then washed with several portions of hexane.

Reaction of $Na^+CpMo(CO)_3^-$ with Allyl Chloride. A THF solution (20 m*l*) of allyl chloride (11.54 mmol) was added to $Na^+CpMo(CO)_3^-$ (0.577 mmol) in a 20 m*l* vol. flask via syringe and was kept in a thermostatted bath at a specific temp. This reaction was monitored by $\nu(CO)IR$ spectroscopy. Usually 10 or more acquisitions of sample were made to get k_{obs} at each specific temp. This reaction was performed at 25°, 30°, 40° and 50°, respectively.

Reaction of $PPN^+CpMo(CO)_3^-$ with Allyl Chloride. A THF soluton (20 m*l*) of allyl chloride (5.77 mmol) was added to $PPN^+CpMo(CO)_3^-$ (0.289 mmol) under the same conditions as in the previous reaction.

Reaction of $M^+CpMo(CO)_3^-$ ($M^+ = Na^+, PPN^+$) with Allyl Bromide. This reaction was performed at 25 °C under the same conditions as in the previous reaction. The reaction was complete within a few min.

Beer's Law Plot (Absorbance vs. Concentration). To each species was added THF (10 m*l*) degassed so as to prepare 5×10^{-3}, 0.5×10^{-3}, 1.0×10^{-3}, 1.5×10^{-3}, and 2.0×10^{-3} M solutions by dilution. The $\nu(CO)IR$ spectra were obtained for each solution for each compound. The base line of transmittance was set to 95%. Attempts wer made to plot the absorbance of each band of one species against its concen-
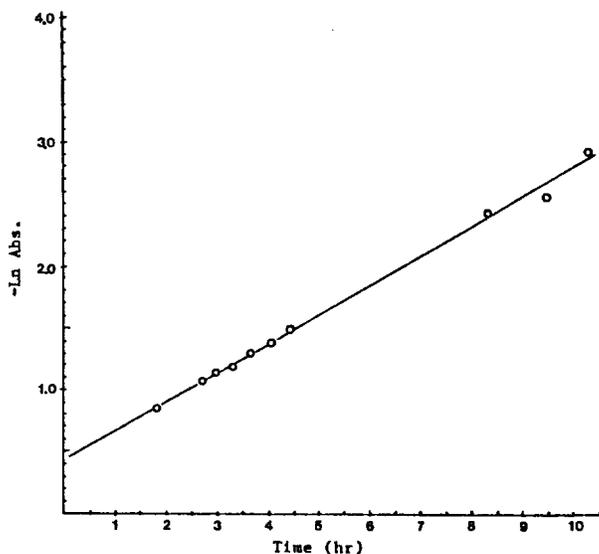
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[a] PPN+ = bis(triphenylphosphine)iminium cation.

Counterion Effect of CpMo(CO)₃⁻ with Allyl Halide

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Figure 1. Pseudo-first-order plot of the reaction of Na⁺CpMo(CO)₃⁺ with $CH_2 = CHCH_2Cl$ (20 fold excess) at 25.0 °C.

tration.

Results and Discussion

Reactions of M⁺CpMo(CO)₃⁻ (M⁺ = Li⁺, Na⁺, K⁺, PPN⁺) with CH₂CHCH₂X (X = Cl, Br). Reactions of M⁺CpMo(CO)₃⁻(M⁺ = Li⁺, Na⁺, K⁺, PPN⁺) with allyl chloride, and allyl bromide were carried out under pseudo-first-order conditions for the metal carbonyl anion with [RX] generally at a 20-fold excess in THF, and monitored with time by ν(CO) IR. Plot of $ln(A_t·A_\infty)$ of the ν(CO)IR band of CpMo(CO)₃⁻ at ca. 1790 cm⁻¹ were linear over the entire reaction (Figure 1). This reaction of CpMo(CO)₃⁻ with CH₂CHCH₂ (X = Cl, Br) in THF produced CpMo(CO)₃ (η^1-CH₂CHCH₂) (ν(CO) IR(THF) 2009(m), 1925(s)) as shown in eq. 2 and the overall second order rate constants for the reaction were obtained. Second order rate rate constants were calculated by dividing k_{obs} by [RX] as in eq. 3.

$$RX + CpMo(CO)_3^- \xrightarrow{k_2} CpMo(CO)_3R + X^- \qquad (2)$$

$$rate = k_2 \, [CpMo(CO)_3^-] \, [RX] \qquad (3)$$

The first-order dependence on allyl halide concentration for the reaction of Na⁺CpMo(CO)₃⁻ with allyl chloride in THF at 25 °C was observed. The observed rate constant was found to have a linear dependence on the allyl chloride concentration with an extrapolated zero intercept over the concentration range between 0.289 and 0.577 M. The reaction of PPN⁺CpMo(CO)₃⁻ with a 20-fold excess of allyl bromide in THF at room temp. was complete within minutes, which strongly indicates that bromide ion is a better leaving group than chloride; therefore, no counterion effect was obtained in this case. In contrast, the reaction of the same nucleophile with a molar equivalent of n-propyl bromide in THF at ambient temp., only approximately 10% of product, CpMo(CO)₃(CH₂CH₂CH₃) (ν(CO) IR 2003(m), 1918(s)) was observed over the course of days.

Determination of Activation Parameters for the Reactions of M⁺CpMo(CO)₃⁻ (M⁺ = Na⁺, PPN⁺) with CH₂ = CHCH₂Cl in THF. The second order rate constants, k_2,

Table 1. Temperature Dependence of Kinetic Data for the Reaction of M⁺CpMo(CO)₃⁻ (M⁺ = Na⁺, PPN⁺)[a] with CH₂ = CHCH₂Cl in THF

Cation	Temp.(°C)	$k_2 \times 10^4, M^{-1}s^{-1}$[b]	Activation Energy parameters[b]
Na⁺	25.0	1.11 ± 0.17	
	30.0	2.23 ± 0.16	$\Delta H^\ddagger$ = 15.50 ± 1.28(KCal/mol)
	40.0	5.10 ± 0.35	$\Delta S^\ddagger$ = −28.7 ± 4.3(e.u.)
	50.0	10.83 ± 0.61	
PPN⁺	25.0	1.01 ± 0.02	
	30.0	1.67 ± 0.04	$\Delta H^\ddagger$ = 14.16 ± 1.54(KCal/mol)
	40.0	3.24 ± 0.02	$\Delta S^\ddagger$ = −33.7 ± 5.2(e.u.)
	50.0	7.30 ± 0.14	

[a][M⁺CpMo(CO)₃⁻] = 0.0145 M [CH₂ = CHCH₂Cl] = 0.289 M. [b]Confidence limits at 90%.
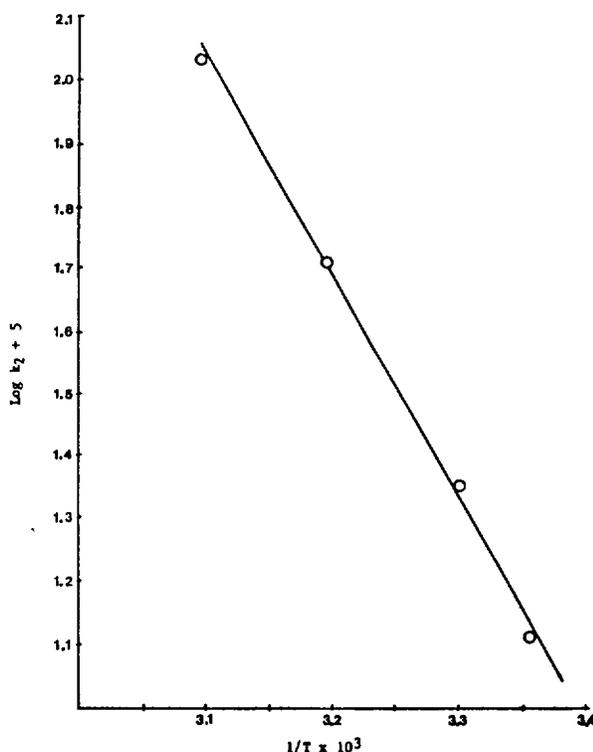
Figure 2. Arrhenius plot for the reaction of Na⁺CpMo(CO)₃⁻ with $CH_2 = CHCH_2Cl$ in THF.

were measured for the reactions of M⁺CpMo(CO)₃⁻ (M⁺ = Na⁺, PPN⁺) with CH₂ = CHCH₂Cl in THF as a function of temperature and the activation parameters were derived from Arrhenius plots. These results are shown in Table 1 and the Arrhenius plots for the reactions of M⁺CpMo(CO)₃⁻ (M⁺ = Na⁺, PPN⁺) with CH₂ = CHCH₂Cl in THF are given in Figures 2 and 3.

The effect of counterions in the reactions of metal carbonylates with organic halides has been studied by several workers.[12] For RX = alkyl halides (i.e., butyl bromide and butyl iodide) a "normal" counterion effect is observed; the less associated the anion is with its counterion, the greater is its nucleophilicity. However, an "inverse" counterion effect has been observed for reactions of RX = activated organic halides such as benzyl chloride or allyl chloride with Co(CO)₄⁻,[3] Mn(CO)₅⁻,[4] and CpMo(CO)₃⁻.[5] In such cases tight ion
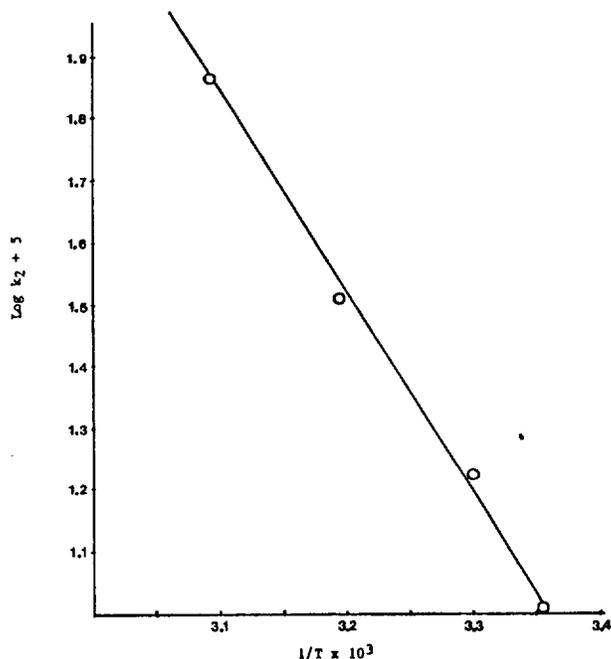
Figure 3. Arrhenius plot for the reaction of PPN $^+$CpMo(CO)$_3^-$ with CH$_2$ = CHCH$_2$Cl in THF.

Comparison of Reaction Rates Between the Reactions of M $^+$ CpMo(CO)$_3^-$ (M $^+$ = Na $^+$, PPN $^+$) with Benzyl Chlorde^6 and the same Nucleophile with Allyl Chloride in THF

Nucleophile	Organic halide	Temp.(°C)	$k_2 \times 10^4, M^{-1}s^{-1}$
Na $^+$CpMo(CO)$_3^-$	C$_6$H$_5$CH$_2$Cl	22	1.94 ± 0.04
PPN$^+$ CpMo(CO)$_3^-$	C$_6$H$_5$CH$_2$Cl	22	0.627 ± 0.019
Na $^+$CpMo(CO)$_3^-$	CH$_2$=CHCH$_2$Cl	25	1.11 ± 0.17
PPN $^+$CpMo(CO)$_3^-$	CH$_2^5$ CHCH$_2$Cl	25	1.01 ± 0.02

pairs enhance the reaction rates. The magnitude of the inverse counterion effect is inversely proportional to the nucleophilicity of the nucleophile; better nucleophile less efficiently experiences the subtle effects of countercations.

$$Fe(CO)_4^{2-}\ CpW(CO)_3^-\ CpMo(CO)_3^-\ CpCr(CO)_3^-\ Co(CO)_4^-$$
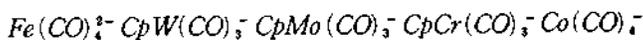
Stronger nucleophile

$\longrightarrow$

More pronounced in inverse counterion effect

In case of the supernucleophile Fe(CO)$_4^{2-}$, solvent-separated ion pairs were more reactive with all organic halides studied than the other nucleophiles above-metioned.^{2}

A 3-fold rate enhancement for the reaction of Na $^+$CpMo (CO)$_3^-$ with benzyl chloride in THF was observed, compared with the reaction of PPN$^+$ CpMo(CO)$_3^-$ with the same organic halide.^{13} However, almost no rate increase was observed for the reaction of Na $^+$CpMo(CO)$_3^-$ with allyl chloride, compared with the reaction of PPN$^+$CpMo(CO)$_3^-$ with allyl chloride in THF as shown in Table 2.

Therefore, it is concluded that not only nucleophilicity of the metal carbonyl anion itself but also the "activated" organic halide electrophile are factors determining the magnitude of the inverse counterion effect and this can be explained in terms of cation assistance of R-X bond cleavage
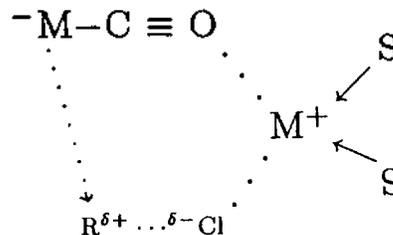

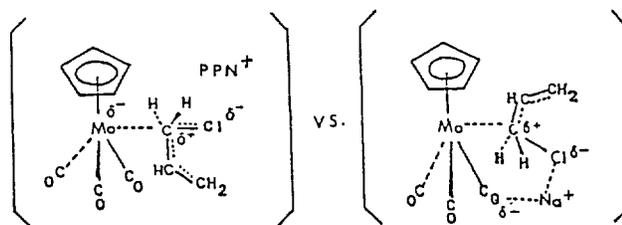**Figure 4.** Counterion (M $^+$) assitance of the leaving group (Cl$^-$). (S: Solvent).

Figure 5. Possible transition states for both PPN $^+$CpMo(CO)$_3^-$ (a) and Na $^+$CpMo(CO)$_3^-$ (b) with allyl chloride in THF.

Table 3. Counterion Dependence of Kinetic Data for Reactions of M $^+$CpMo(CO)$_3^-$ (M $^+$ = Li $^+$, Na $^+$, K $^+$, PPN $^+$) with CH$_2$ = CHCH$_2$Cl in THF at 40°C

Cation	$k_2 \times 10^4, M^{-1}s^{-1}$
Li $^+$	6.60 ± 1.07
Na $^+$	5.10 ± 0.35
K $^+$	6.04 ± 0.46
PPN $^+$	3.24 ± 0.02

where the RX molecule has some carbonium ion character or some charge separation as shown in Figure 5.^{4}

It is also likely that the reactivity is doubly benefitted by both the cation leaving group assistance due to R$^{\sigma+}$-X$^{\sigma+}$...Na$^+$ formation as well as by keeping RX into a close proximity for M-R bond formation. It must be kept in mind that this inverse counterion effect is always in competition with the normal counterion effect in such reactions. The tight ion pair weakens the nucleophilicity of the metal carbonyl anion. Therefore, in case of the reaction of M $^+$CpMo(CO)$_3^-$ (M $^+$ = Na $^+$, PPN $^+$) with allyl chloride, these two counterion effects (inverse and normal) compete well, essentially cancelling each other in the reaction (25 °C). In the reaction of M $^+$CpMo(CO)$_3^-$ (M $^+$ ≠ Na $^+$, PPN $^+$) with benzyl chloride, the inverse counterion effect is dominant over the normal counterion effect.

The highly negative entropy change of activation in both the reactions of Na $^+$CpMo(CO)$_3^-$ and PPN$^+$CpMo(CO)$_3^-$ with allyl chloride suggests a great amount of order in the transition state of the reactants, which indicates a charge dispersion as illustrated in Figure 5.

Counterions such as Li $^+$ and K $^+$ as well as Na $^+$ were observed to promote reaction rates of CpMo(CO)$_3^-$ with allyl chloride to similar magnitude over that of PPN$^+$CpMo (CO)$_3^-$. The slight differences between Li $^+$ and K $^+$ as well as Na $^+$ are statically insiginificant (Table 3).

Solvent Effect. Several solvents such as CH$_3$CN, THF, and DME were used to determine the solvent effect on the

Table 4. Solvent Dependence of Rates of Reaction of M^+ CpMo(CO)₃⁻ (M^+ = Na⁺, PPN⁺) with CH₂ = CHCH₂Cl at 40°C

Solvent(ε)	M^+	$k_2 \times 10^4$, $M^{-1}s^{-1}$	$\dfrac{k_2(\text{PPN}^+)}{k_2(\text{Na}^+)}$
CH₃CN(36.2)	PPN⁺	~160 *(t-2.5 min.)	~17
	Na⁺	9.58 ± 0.37	
THF (7.32)	PPN⁺	3.24 ± 0.02	~0.6
	Na⁺	5.10 ± 0.35	
DME (3.49)	PPN⁺	3.71 ± 0.74	~0.8
	Na⁺	4.48 ± 0.24	

*This reaction was over within 20 min so that the accurate k_2 could not be obtained by ν(CO) IR absorbance measurements.

rate of reaction of M^+CpMo(CO)₃⁻ (M^+ = PPN⁺, Na⁺) with allyl chloride.

Usually polar solvent molecules better solvate small cations such as Na⁺ so that in the absence of specific leaving group assistance, the reactive anion in the palar solvent CH₃CN becomes more nucleophilic than in THF. Therefore the reaction of Na⁺CpMo(CO)₃⁻ with allyl chloride in CH₃CN should be enhanced compared to that in less polar solvents such as THF or DME as shown in Table 4.

The good solvation between polar solvent molecules and small cation (Na⁺) may hinder the possible interaction between the coordinated CO and the cation. At the transition state Cl atom will become quite polarized (Cl$^{σ-}$) so that it can compete better for Na⁺ than the polar solvent molecule. Therfore more interaction between Na⁺···Cl$^{σ-}$ is expected. This reasoning of Na⁺···Cl$^{σ-}$ interaction may be more plausible by the so-called Hammond postulate[15] which states that in an endothermic reaction the geometry of the transition state resembles the high-energy product. In very polar solvent CH₃CN (ε = 36.2) the reaction of PPN⁺CpMo(CO)₃⁻ with allyl chloride is almost 40~50 times faster than the same reactions in either THF (ε = 7.32) or DME (ε = 3.49). k_2 (PPN⁺)/k_2(Na⁺) in Table 4 shows that in polar solvent in this reaction of PPN⁺CpMo(CO)₃⁻ with allyl chloride the inverse counterion effect is not working; however, in the slight polar solvent such as THF or DME this inverse countrion effect is playing a major role in the reaction rate enhancement.

Mode of Attack by Na⁺CpMo(CO)₃⁻ on Crotyl Bromide. In an effect to examine the possibility of remote attack of the nucleophile on allyl halide, the reaction of Na⁺ CpMo(CO)₃⁻ with crotyl bromide (BrCH₂CH = CHCH₃) in THF at room temp. was studied. The observed product was CpMo(CO)₃(CH₂CH = CHCH₃) (ν(CO) IR, 2003(s), 1920(s); ¹H NMR(d⁸-toluene) δ 6.10-5.56(1H, m), 5.60-5.20(1H, m), 4.77(5H, s), 2.43(2H, d), 1.82(2H, d)) rather than CpMo(CO)₃ (CH(CH₃)CH = CH₂). This structural interpretation of CpMo (CO)₃(CH₂CH = CHCH₃) was based on the ¹H NMR spectra comparison between ClCH₂CH = CHCH₃(¹H NMR(CD₃Cl), δ1.71(3H, d), 4.02(2H, d), 5.60(1H, m), 5.78(1H, m)), and ClCH(CH₃)CH = CH₂ (¹H NMR(CCl₄), δ1.56(3H, d), 4.43(1H, quint.), 5.89(1H, m), 5.03(1H, m))[16b].

The ¹H NMR pattern for CpMo(CO)₃(CH₂CH = CHCH₃) is quite similar to ClCH₂CH = CHCH₃. Both compounds have two doublets and both of them do not have the quintet which

the isomer ClCH₂CH = CHCH₃ has at δ 4.43 ppm. The latter ClCH(CH₃)CH = CH₂ also has only one peak at δ 1.56 ppm. Such differences clearly indicate that the product from the reaction of Na⁺CpMo(CO)₃⁻ with crotyl bromide is CpMo (CO)₃(CH₂CH = CHCH₃).

Thus, the nucleophile seems to attack the α-carbon adjacent to the halide, not the γ-carbon attached to CH₃ group. However, the CH₃ group substituent on the γ-carbon in crotyl bromide would make that carbon more electron rich than the analogous γ-carbon in allyl bromide. That is the γ-carbon in crotyl bromide may be slightly less acidic than the terminal or γ-carbon of allyl bromide. This argument then might weaken the validity of the conclusion that nucleophile is more likely to attack the carbon next to halide than the terminal carbon of allyl bromide.

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16. (a) ¹H NMR spectral data (for *trans*-1-chloro-2-butene) were obtained from ¹H NMR (27110M), Sadtler Standard NMR Spectra; (b) ¹H NMR spectral data (for 3-chloro-1-butene) were obtained from ¹H NMR (21618 M), Sadtler Standard NMR Spectra. Sadtler Research Laboratories.