

Figure 2. Plot of the rate of reaction of $\text{Cr}(\text{CO})_5$ (●) and the rate of reformation of $\text{Cr}(\text{CO})_6$ (○) as a function of added CO. Parent pressure and buffer gas pressure were the same as in Figure 1. Both give the same rate within experimental error, and thus the slope of the data points is indicated as a single line.

and 1948 cm^{-1} (features 2 and 3), which grow in to a near maximum amplitude 500 ns after excitation, are assigned to the e and low-frequency a_1 vibrations of $\text{Cr}(\text{CO})_5$. The remaining high-frequency CO stretching vibration is not within the range of our probe laser. The existence of two $\text{Cr}(\text{CO})_5$ absorptions, their approximate relative intensity ratio, and their correlation within experimental error to absorptions observed for $\text{Cr}(\text{CO})_5$ in a neon matrix, where a significant matrix shift vs. the gas phase is not expected, imply that $\text{Cr}(\text{CO})_5$ in the gas phase has the same square-pyramidal C_{4v} geometry as assigned to matrix isolated $\text{Cr}(\text{CO})_5$.

It is evident from Figure 1 that the intensity of the 1980-cm^{-1} absorption (feature 2) is approximately $2/3$ that of the 2000-cm^{-1} band (feature 1). This is in accord with expectations based on simple intensity arguments, with the implicit assumption that the major product of $\text{Cr}(\text{CO})_6$ photolysis is $\text{Cr}(\text{CO})_5$. The large relative yield of $\text{Cr}(\text{CO})_5$ at this photolysis wavelength is consistent with the observations of Breckenridge and Sinai.⁶ The weaker features in Figure 1 (not labeled) can most likely be assigned to small amounts of $\text{Cr}(\text{CO})_4$. The features attributed to the gas-phase absorptions of both $\text{Cr}(\text{CO})_5$ and $\text{Cr}(\text{CO})_4$ are, as expected, blue-shifted by similar amounts relative to their position in an argon matrix.^{12,13}

Existing data imply that the energy of a 351-nm photon (82 kcal mol^{-1}) is just sufficient to remove two CO groups.¹⁴ This could account for the low yield of products other than $\text{Cr}(\text{CO})_5$ at this wavelength. Experiments, currently under way, show that fragments other than $\text{Cr}(\text{CO})_5$ can be generated by increasing the energy of the incident photon.¹⁵ This is consistent with chemical trapping studies.⁷

The identification of $\text{Cr}(\text{CO})_5$ was confirmed by correlating its rate of decay (features 2 and 3) with the rate of reappearance of $\text{Cr}(\text{CO})_6$ (feature 1) as a function of added CO. Figure 2 shows that the rate for both processes is concurrent within experimental error. From the slopes of the lines the rate constant for reaction

of $\text{Cr}(\text{CO})_5$ with CO was determined as $(1.5 \pm 0.3) \times 10^{13}\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$ ($800 \pm 150\text{ ms}^{-1}\text{ torr}^{-1}$). (The error brackets represent the 95% confidence values.) Moreover, the same rate constant was obtained under a variety of conditions, i.e., with and without added He or Ar, both in a flow cell and in a static cell. This implies that any complex formation with added rare gas is minimal and certainly does not affect the recombination kinetics.

In solution $\text{Cr}(\text{CO})_5$ is known to be highly reactive.³⁻⁵ We note that in the gas phase the rate constant for reaction of $\text{Cr}(\text{CO})_5$ with CO is more than 2 orders of magnitude higher than the corresponding rate for reaction of $\text{Fe}(\text{CO})_4$ with CO ($(3.5 \pm 0.9) \times 10^{10}\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1}$).¹⁰ This difference can be, at least in part, rationalized in terms of $\text{Fe}(\text{CO})_4$ having a triplet ground state,¹⁶ whereas the $\text{Cr}(\text{CO})_5$ ground state is almost certainly a singlet.¹⁷ Steric conditions may also play a role in the large difference in rates.

Using relative band-intensity arguments, kinetic evidence, and agreement with absorption frequencies of matrix-isolated $\text{Cr}(\text{CO})_5$, we have assigned the infrared absorptions observed subsequent to 351-nm photolysis of $\text{Cr}(\text{CO})_6$ to the pentacarbonylchromium fragment. These experiments have also essentially confirmed that the structure of "naked" $\text{Cr}(\text{CO})_5$ is square pyramidal, a result consistent with simple molecular orbital calculations.¹⁷

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Isotopic Multiplets in the ^{13}C NMR Spectra of Partially Deuterated Ammonium Derivatives. Spectral Effects of Isotopic Asymmetry at a Nitrogen Atom[†]

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Concurrent communications from two laboratories have recently demonstrated that the isotopic multiplets observed in the proton-decoupled ^{13}C NMR spectra of carbohydrates with partially deuterated hydroxyls can be very helpful in spectral assignments^{1,2} and molecular structure determinations.³ These multiplets are due to upfield deuterium isotope effects on the ^{13}C chemical shifts⁴ and can be observed when hydrogen exchange is slow relative to the magnitude of the isotope effect. Deuterium isotope effects have also been reported for amine, amide, and amino acid systems.⁵⁻⁹ The slow exchange of amide hydrogens has led to the

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Table I. Carbon-13 Chemical Shifts (in ppm),^a Multiplicities,^b and Deuterium Isotope Effects (in ppb/deuteron) for Protonated Amines

| | C1 | C2 | C3 | C4 | C5 | C6 | C7 |
|---|---------------------------------|------------------------------------|----------------------|-----------------------|----------------|----------------|----------------|
| H ₂ NCH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ CH ₂ NH ₂ spermidine ^c | 37.93 q; 94 | 24.92 q; t; 40, 30 ^e | 46.76 t; 91 | 48.28 t; 90 | 23.82 t; 30 | 25.09 q; 46 | 40.16 q; 97 |
| [(CH ₃) ₂ CH] ₂ NH diisopropylamine ^d | 20.33 t; 31 ^g | 47.90 t; 58 | | | | | |
| (CH ₃) ₂ CHNHCH ₂ CH ₃ ethylisopropylamine ^d | 20.43 d,d; 36 ^{f,g} | 50.79 t; 66 | 40.88 t; 79 | 12.99 t; 36 | | | |
| (CH ₃) ₂ CHNHCH ₂ C(CH ₃) ₂ NH ₂ <i>N'</i> -isopropyl-2-methyl-1,2-propanediamine ^d | 20.02 d; 25 ^e | 53.22 t; 55 | 52.67 t,q; 76, 25 | 54.16 q, t; 62, 28 | 25.46 q; 43 | | |
| HOOCCH(NH ₂)CH ₂ CH ₂ CH ₂ CH ₂ NH ₂ L-lysine ^d | 172.35 q; 42 | 53.34 q; 65 | 30.89 q; 45 | 23.05 | 27.93 q; 51 | 39.96 q; 87 | |

^aCarbon atoms are numbered consecutively from left to right. ^bd = doublet, t = triplet, q = quartet. ^cIn an acidified 1:1 H₂O/D₂O mixture; dioxane as an internal reference at 67.4 ppm. ^dIn Me₂SO-*d*₆ containing acidified H₂O/D₂O mixtures; the central peak of the solvent as an internal reference at 41.1 ppm. ^eObtained by a computer simulation. ^fThe separation of the inner components is 33 ppb. ^gDiastereotopic methyls in the NHD⁺ form (see text).

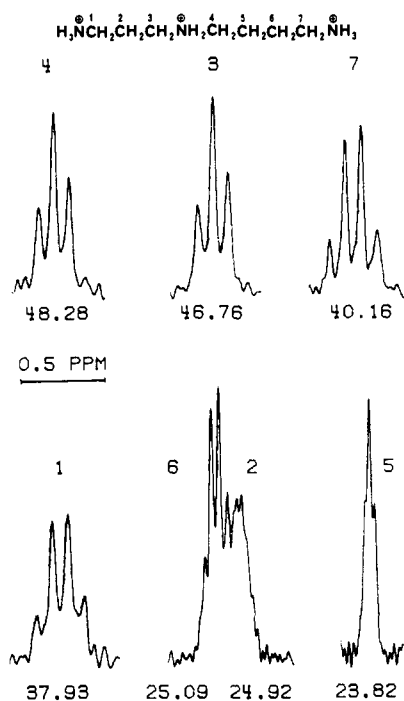


Figure 1. Isotopic multiplets in the ¹³C NMR spectrum (at 90.56 MHz) of spermidine in an acidified ca. 1:1 H₂O/D₂O mixture. Chemical shift values (in ppm) are for the protio form (low-field component).

observation of isotopic multiplets in the spectra of amides.^{5,7,8} However, the isotopic multiplets in the spectra of amines have remained largely unexplored.¹⁰

Partial deuteration of protonated amines, i.e., ammonium ion derivatives, can be achieved in acidified H₂O/D₂O mixtures, either in an aqueous medium or in Me₂SO solutions. According to the classic work of Grunwald, Lowenstein, and Meiboom, hydrogen exchange in such systems is expected to be slow on the NMR time scale.¹¹ As a result, the isotope effects on the ¹³C chemical shifts of the α- and β-carbons (ca. 0.09 and 0.03 ppm/deuteron, respectively⁶) should give rise to distinct ¹³C resonances for the individual isotopomers. Figure 1 presents, as an example, the isotopic multiplets in the ¹³C NMR spectrum of spermidine in an acidified 1:1 H₂O/D₂O mixture. The spectrum of spermidine has recently been assigned by Kimberly and Goldstein.¹² However, the assignments of carbons 2 and 6 in the fully protonated form have remained ambiguous. The isotopic multiplets readily resolve this ambiguity. Owing to the analogy between the isotopic

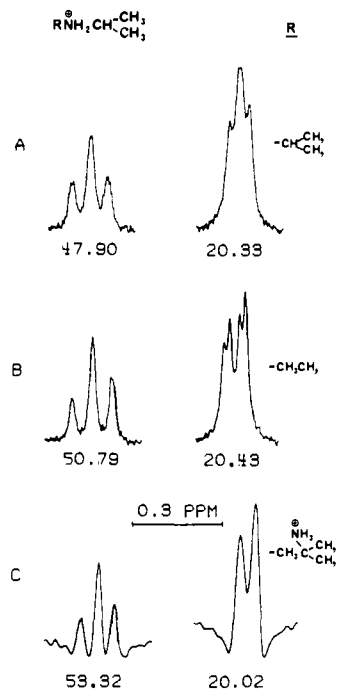


Figure 2. Isotopic multiplet in the ¹³C resonances (at 90.56 MHz) of the isopropyl groups of amines in Me₂SO-*d*₆ containing acidified H₂O/D₂O mixtures. Chemical shift values (in ppm) are for the protio form (low-field component): (A) diisopropylamine, (B) ethylisopropylamine, (C) *N'*-isopropyl-2-methyl-1,2-propanediamine.

state of a hydrogen ("light" or "heavy") and the spin state (+1/2 or -1/2) of a spin 1/2 nucleus in a magnetic field, there is a similarity between isotopic multiplets and those due to spin-spin couplings.¹ Thus, carbons 1 and 7, α to NH₃⁺ groups, are quartets, the components of which correspond to the NH₃⁺, NH₂D⁺, NHD₂⁺, and ND₃⁺ species. Carbons 3 and 4, α to the NH₂⁺ groups, are triplets. Carbon 5, β to the NH₂⁺ group, is also a triplet but with smaller spacings. The resonance of carbon 6 is expected to be a quartet with relatively small spacings, since this atom is β to a NH₃⁺ group. Carbon 2 should exhibit higher multiplicity, since this atom is β to NH₃⁺ and NH₂⁺ groups. Thus, the multiplets with low-field components at 25.09 and 24.92 ppm (see Figure 1) are unequivocally assigned to carbons 6 and 2, respectively.

The chemical shift values and the magnitudes of the isotope effects for spermidine, as well as for the other substances investigated in this work, are summarized in Table I. The two-bond isotope effect is in the range 0.055–0.097 ppm/deuteron. Values at the lower end of this range are observed with higher substitution on the nitrogen or carbon atoms. The three-bond isotope effect is in the range 0.025–0.051 ppm/deuteron. Again higher substitution leads to lower values. Noteworthy in this respect is carbon 2 of spermidine. Its resonance is affected by three-bond isotope effects from NH₃⁺ and NH₂⁺ groups. The magnitude of these

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effects are 0.04 and 0.03 ppm, respectively. Thus, the magnitude of the isotope effect should be useful in spectral assignments.

An interesting phenomenon was observed with secondary ammonium ions of the type $A(NH_2^+)B$. The nitrogen atom in the monodeuterated species of such ions, $A(NHD^+)B$, is asymmetric. Therefore, if one of the substituents is isopropyl, e.g., $(CH_3)_2CHNH_2^+R$, the originally enantiotopic and isochronous isopropyl methyls become diastereotopic and anisochronous in the $(CH_3)_2CHNHD^+R$ species. This phenomenon is illustrated in Figure 2. For the partially deuterated diisopropylammonium ion both the CH and CH_3 resonances appear as triplets with large and small spacings, respectively (Figure 2A). However, for the ethylisopropylammonium ion the isopropyl methyls give rise to a clearly resolved quartet (Figure 2B). The spacing between the inner components of this quartet corresponds to the chemical shift difference (0.033 ppm) between the diastereotopic isopropyl methyls in the monodeuterated species. In the N' -isopropyl-2-methyl-1,2-propanediammonium ion this difference is approximately equal to the chemical shift (0.049 ppm) between the protio and deuterio forms, resulting in a doublet (Figure 2C). On the other hand, in the diisopropyl case the chemical shift between the diastereotopic methyls is smaller than the line-width (0.015 ppm), giving rise to a triplet (Figure 2A).

For amino acids and their derivatives, partial deuteration of the α ammonium group gives rise to isotopic multiplets in the carboxyl as well as in the backbone carbon resonances. Thus, isotopic multiplets should be useful in the assignment of such resonances and in the identification of terminal residues of peptides.

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Registry No. $H_3N(CH_2)_3NH_2(CH_2)_4NH_3^{3+}$, 74676-62-3; $[(CH_3)_2CH]_2NH_2^+$, 21445-72-7; $(CH_3)_2CHNH_2CH_2CH_3^+$, 94041-96-0; $(CH_3)_2CHNH_2CH_2C(CH_3)_2NH_3^{2+}$, 94859-78-6; L-HOOCCH(NH₂)-(CH₂)₄NH₃²⁺, 17829-44-6; D₂, 7782-39-0.

Stereoelectronic Controlling Features of Allylic Asymmetry. Application to Ester Enolate Alkylations

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Asymmetric transformations of unsaturated species have attracted considerable synthetic and theoretical interest.^{1,2} An intriguing facet of the chemistry of **1** is the manner through which the asymmetric center renders the faces of the adjacent π -system chemically nonequivalent. Kinetic stereoselection in species **1** has been attributed to a number of conformational models that are conveniently classified as being eclipsed (A-D) or perpendicular (E-H, Figure 1).^{1c,d} We present herein support for a transition-state model for electrophilic additions that is based upon conformer H, which finds considerable generality in predicting the stereochemical outcome of asymmetric reactions in this class.

Calculations modeling the transition states for the reaction of simple substrates with nucleophiles, electrophiles, radicals, and dipoles indicate a pronounced preference for perpendicular geometries in all cases.^{1a,b} The approaching reagent is generally

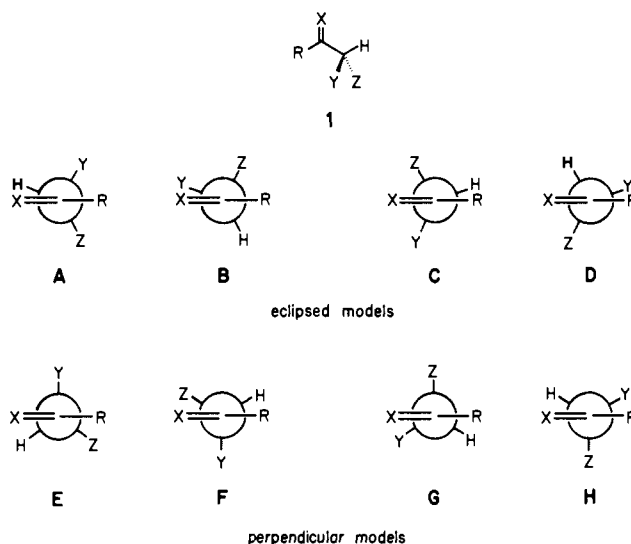


Figure 1.

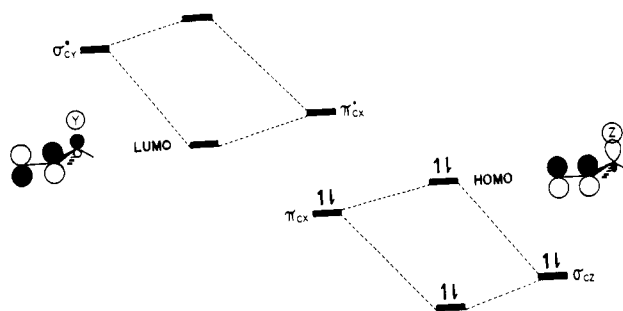


Figure 2.

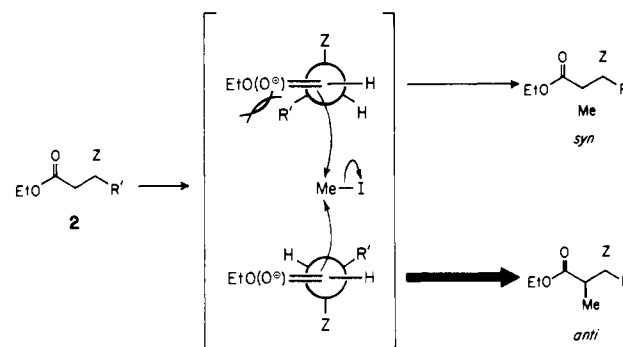


Figure 3.

directed antiperiplanar to the perpendicularly disposed substituent through secondary orbital interactions.¹⁻³ These theoretical conclusions find no contradictions in a rapidly growing body of experimental evidence. This being the case, the description of a given transition state requires the deployment of the appropriate substituent in the proper perpendicular position. In the MO formalism,⁴ nucleophilic attack will seek the LUMO of the electrophile. This may be favorably affected through mixing of the π^* orbital with the lowest energy σ^* orbital, which is associated with the most electronegative substituent (e.g., Y; Figure 2).⁵ In the event of electrophilic attack, however, the substrate's HOMO governs the course of the reaction. In this instance, the π orbital mixes with the highest energy σ orbital, belonging to the substituent that most efficiently participates in hyperconjugative

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