

(CHCl<sub>3</sub>-6% MeOH); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +231.6° (*c* 1.5, CHCl<sub>3</sub>); UV (MeOH)  $\lambda$  283 (log  $\epsilon$  4.16) and 225 nm (sh, log  $\epsilon$  4.17); IR (NaCl)  $\nu$  3415, 2930, 2890, 2825, 1690, 1658, 1627, 1411, 1381, 1329, 1234, 1125, 1077, 1050, 935, 842 cm<sup>-1</sup>; mass spectrum, *m/z* (relative intensity) 328 (M<sup>+</sup>, 5%), 310 (3), 295 (2), 285 (4), 271 (5), 267 (3), 255 (10), 230 (9), 205 (301), 204 (23), 191 (15), 189 (14), 147 (8), 125 (13), 105 (12), 91 (24), 85 (26), 83 (41), 81 (77), 53 (92), 43 (100), 28 (38). Mass measurement, C<sub>20</sub>H<sub>24</sub>O<sub>4</sub> requires 328.1674; found 328.1665.

**Trichloroacetyl Carbamate of Hydroxyjatrophone A.** To a solution of 2 $\alpha$ -hydroxyjatrophone (3 mg) in CDCl<sub>3</sub> (0.2 mL) was added one drop of trichloroacetyl isocyanate and the solution was subjected to NMR measurement. After evaporation of the solvent, the crystalline residue was recrystallized from acetone to afford 3 mg of product, mp 156.2-156.3 °C: IR (KBr) 2.95, 5.52, 5.88, 6.00, 6.18, 6.6, 8.55, 12.0  $\mu$ ; NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  8.36 (1 H, s, NH), 6.46 (1 H, d, *J* = 16 Hz, 9-H), 6.07 (1 H, m, 3-H), 6.00 (1 H, d, *J* = 16 Hz, 8-H), 5.79 (1 H, m, 5-H), 2.91 (1 H, d, *J* = 15.4 Hz, 11-H $\alpha$ ), 2.76 (1 H, d, *J* = 14 Hz, 1-H), 2.51 (1 H, d, *J* = 15.4 Hz, 11-H $\beta$ ), 2.47 (1 H, d, *J* = 14 Hz, 1-H), 1.92 (3 H, d, *J* = 2 Hz, 17-CH<sub>3</sub>), 1.74 (6 H, s, 16-CH<sub>3</sub>), 1.38 (3 H, s, 19-CH<sub>3</sub>), 1.25 (3 H, s, 18-CH<sub>3</sub>); mass spectrum, *m/e* 310 (M<sup>+</sup> - CCl<sub>3</sub>CONHCOOH), 295, 282, 267, 239, 226, 211, 186, 150, 128, 115, 91.

**Nuclear Overhauser Enhancement Difference Spectra (NOEDS).** The procedure employed was similar to that described by Hall and Sanders.<sup>15,16</sup> Samples of the jatrophones (2-25 mg) were dissolved in deuteriochloroform, degassed by five freeze-thaw cycles at 10<sup>-3</sup> torr, and then sealed under vacuum.

Spectra were obtained at 250 MHz with 8K data points. Ten transients were taken with irradiation at the on-resonance frequency, the memory was negated, ten more transients were collected with irradiation at the off-resonance frequency, and memory was again negated. The first

two transients in each set were not accumulated to allow equilibration. The sequence was repeated 8 to 256 times until satisfactory signal to noise levels were obtained. The decoupler power level was adjusted until a single resonance was irradiated.

From the difference spectrum the magnitude of the NOE could be determined from the absolute values of the integration of the enhanced resonance and the irradiated resonance, which was assumed to be 100%.

**Two-Dimensional J-Resolved Spectra.** The spectra were obtained at 200 MHz on an IBM WM-200 spectrometer following a procedure similar to that described by Hall and Sanders.<sup>15,16</sup> A spectral width of 500 Hz covering the high-field region of the spectrum was examined over 2K data points (digital resolution of 0.24 Hz). Data processing using software provided by Bruker was performed on 128 spectra of 16 transients each with *t* incremented by 16 ms, which each time gave an *F*<sub>1</sub> width of 31.0 Hz with resolution of 0.12 Hz.

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## Mechanisms of Elimination Reactions. 36. Stereochemistry and Transition-State Structure in Eliminations from Primary Alkyltrimethylammonium Salts<sup>1,2</sup>

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**Abstract:** A study of stereochemistry of elimination in E2 reactions of R<sub>1</sub>R<sub>2</sub>CHCHDNMe<sub>3</sub><sup>+</sup> reveals that syn elimination can become the major reaction path when R<sub>1</sub> and R<sub>2</sub> are both bulky groups such as aryl or branched alkyl. With OH<sup>-</sup>/50% Me<sub>2</sub>SO-H<sub>2</sub>O at 80 °C, the percent of syn is 68.5 for R<sub>1</sub> = Ph, R<sub>2</sub> = *i*-Pr; 61.9 for R<sub>1</sub> = Ph, R<sub>2</sub> = *p*-MeOPh; 26.5 for R<sub>1</sub> = Ph, R<sub>2</sub> = CH<sub>3</sub>. With *n*-BuO<sup>-</sup>/50% Me<sub>2</sub>SO-*n*-BuOH, the percent of syn runs 61.5 for R<sub>1</sub> = Ph, R<sub>2</sub> = *i*-Pr; 12 for R<sub>1</sub> = *n*-Bu, R<sub>2</sub> = Me; and <5 for R<sub>1</sub> = *n*-Bu, R<sub>2</sub> = D. The results can be rationalized by a simple conformational argument in which steric interactions between bulky  $\beta$ -substituents and the leaving trimethylammonio group destabilize the transition state for anti elimination. Primary  $\beta$ -tritium, secondary  $\alpha$ -tritium, and primary  $\alpha$ -<sup>14</sup>C isotope effects were determined on the (2,2-diphenylethyl)trimethylammonium ion and compared with similar data on the (2-phenylethyl)trimethylammonium ion, which eliminates by an exclusively anti mechanism. The extent of proton transfer in the transition state seems not to differ widely between the two systems, but the extent of C-N cleavage appears less in the 2,2-diphenylethyl system. Hammett  $\rho$  values are smaller in the 2,2-diphenylethyl system, though their interpretation presents ambiguities.

Our initial aim in these studies was to compare transition-state structure and the propensity for tunneling in eliminations from 2-arylethyl and 2,2-diarylethyl derivatives.<sup>4</sup> When we studied the quaternary ammonium salts in these and related systems however, we became increasingly convinced that simple differences in transition-state structure were not sufficient to explain the

differences in the results. We then set out to examine the stereochemistry of elimination using appropriate stereospecifically deuterated derivatives. Prior studies with 2-phenylethyl-1,2-*d*<sub>2</sub>-trimethylammonium<sup>5</sup> and 1-decyl-1,2-*d*<sub>2</sub>-trimethylammonium<sup>6</sup> ions revealed little or no syn elimination from primary alkyltrimethylammonium ions in protic solvents. No work with  $\beta$ -branched primary alkyl derivatives had been reported, however.<sup>7</sup>

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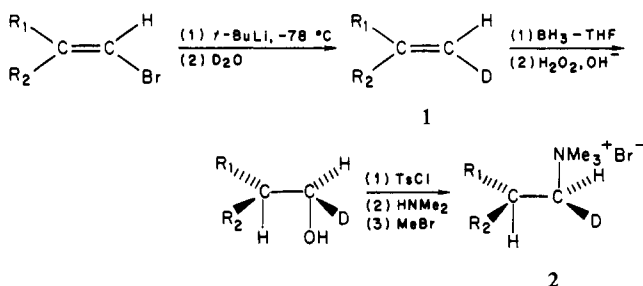
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Scheme I. Synthesis of Stereospecifically Deuterium-Labeled Substrates

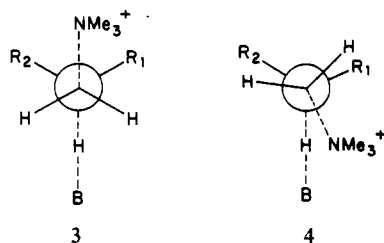


The general procedure for synthesis of the stereospecifically deuterium-labeled substrates is shown in Scheme I. The vinyl bromides were obtained by brominating the corresponding olefins and dehydrobrominating the resulting dibromides, followed by separation of the *E* and *Z* isomers by recrystallization, chromatography, or careful fractional distillation. The initial stages of the synthesis of 1-hexyl-1,2-*d*<sub>2</sub>-trimethylammonium ion were different. (*Z*)-1-Hexene-1-*d* resulted from hydroboration and protolysis of 1-hexyne-1-*d*, while (*E*)-1-hexene-1-*d* was obtained by hydroboration and deuterolysis of 1-hexyne.<sup>8,9</sup> The remainder of the synthesis involved deuterioboration and oxidation of the borane to the alcohol, which was then converted to the quaternary ammonium salt as in Scheme I.

It is apparent that anti elimination from the quaternary ammonium salt **2** in Scheme I will give deuterated olefin of the same stereochemistry as that used in the synthesis, **1**, while syn elimination will give the stereoisomeric olefin. The isomeric olefins were readily differentiated by 400-MHz <sup>1</sup>H NMR spectroscopy in all cases and by 100-MHz NMR spectroscopy in some. While the absolute stereochemistry of the deuterated olefins need not be known to deduce the stereochemical course of the elimination, we believe our stereochemical assignments (see the Experimental Section for details) are sound.

The results of our stereochemical studies are recorded in Table I. The pattern is quite clear. Two aryl groups or an aryl and an isopropyl group on the β-carbon give predominant syn elimination, while an aryl and a methyl group give predominant but not exclusive anti elimination. Still less syn elimination results when the β-substituents are *n*-butyl and methyl, and syn elimination is negligible when they are *n*-butyl and hydrogen.

To a good approximation, the propensity for syn elimination depends upon the steric requirements of the β-substituents, with two β-substituents needed to bring about appreciable syn elimination in protic solvents. This pattern is entirely consistent with a simple steric explanation in which interaction of the β-substituents with the bulky leaving group destabilizes the transition state for anti (3) more than that for syn (4) elimination. The anti



transition state for the substrates where  $R_1$  = alkyl or aryl and  $R_2$  = H can reduce these unfavorable interactions by twisting slightly out of the anti-periplanar conformation, while such twisting where both  $R_1$  and  $R_2$  = alkyl or aryl can relieve one interaction only at the expense of making the other worse.

The overall rates of elimination of  $\text{PhRCHCH}_2\text{NMe}_3^+$  with hydroxide ion in 50% dimethyl sulfoxide–water at 80 °C are 2.96

Table I. Stereochemistry of Elimination from  $\text{R}_1\text{R}_2\text{CHCHDNMe}_3^+\text{Br}^-$ 

$R_1$	$R_2$	base/solvent <sup>a</sup>	$T$ , °C	% syn
$\text{C}_6\text{H}_5$	$(\text{CH}_3)_2\text{CH}$	$\text{OH}^-/50\% \text{ Me}_2\text{SO}-\text{H}_2\text{O}$	80	68.5
		$n\text{-BuO}^-/50\% \text{ Me}_2\text{SO}-n\text{-BuOH}$	80	61.5
$\text{C}_6\text{H}_5$	$p\text{-CH}_3\text{OC}_6\text{H}_4$	$\text{OH}^-/50\% \text{ Me}_2\text{SO}-\text{H}_2\text{O}$	80	61.9
			40	57.7
$\text{C}_6\text{H}_5$	$\text{CH}_3$	$\text{OH}^-/50\% \text{ Me}_2\text{SO}-\text{H}_2\text{O}$	80	26.5
$\text{C}_6\text{H}_5$	D	$\text{EtO}^-/\text{EtOH}$	60	<5 <sup>b</sup>
		$t\text{-BuO}^-/t\text{-BuOH}$	60	<5 <sup>b</sup>
$n\text{-C}_4\text{H}_9$	$\text{CH}_3$	$n\text{-BuO}^-/50\% \text{ Me}_2\text{SO}-n\text{-BuOH}$	80	12
$n\text{-C}_4\text{H}_9$	D	$n\text{-BuO}^-/50\% \text{ Me}_2\text{SO}-n\text{-BuOH}$	80	<5
$n\text{-C}_8\text{H}_{17}$	D	$t\text{-BuOK}/t\text{-BuOH}$	100	7 <sup>c</sup>
		$t\text{-BuOK}/\text{C}_6\text{H}_6$	80	19 <sup>c</sup>

<sup>a</sup> Solvent composition in mol %. <sup>b</sup> From ref 5. <sup>c</sup> From ref 6.

Table II. Primary  $k_{\text{H}}/k_{\text{T}}$  Values for E2 Reactions of  $\text{Ph}_2\text{CTCH}_2\text{NMe}_3^+\text{I}^-$  with  $\text{OH}^-$  in  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ 

$\text{Me}_2\text{SO}$ , mol %	$T$ , °C	$k_{\text{H}}/k_{\text{T}}^a$	$k_{\text{H}}/k_{\text{D}}^c$
30	50	10.4	5.1
40	50	12.0	5.6
50	50	13.0	5.9
60	50	13.3	6.0
30	20	16.6 <sup>b</sup>	7.0
40	20	16.0	6.9
50	20	16.8	7.1
60	20	16.8	7.1
70	20	17.8	7.4
80	20	19.9	8.0

<sup>a</sup> Average of two runs. <sup>b</sup> Extrapolated from Arrhenius parameters of data at 40–80 °C. <sup>c</sup> Calculated from  $k_{\text{H}}/k_{\text{D}} = (k_{\text{H}}/k_{\text{T}})^{1/1.44}$  (ref 10).

$\times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  for  $\text{R} = \text{Me}$  and  $1.43 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  for  $\text{R} = i\text{-Pr}$ . Combining these figures with the fractions of syn elimination from Table I gives  $(k_{\text{Me}}/k_{i\text{-Pr}})_{\text{syn}} = 8.0$  and  $(k_{\text{Me}}/k_{i\text{-Pr}})_{\text{anti}} = 48$ . The change from methyl to isopropyl slows both syn and anti elimination, probably by steric and/or electronic effects on the ease of proton removal, but anti elimination is slowed by a much larger factor. This extra effect of isopropyl on the anti elimination is plausibly accounted for by the steric explanation in the preceding paragraph.

Our results so far can be accounted for entirely by this explanation. The similar effects of isopropyl and aryl groups on the stereochemistry of elimination suggest that electronic influences are secondary. Nonetheless, we intend to explore the effects of meta and para substituents in the aromatic ring on stereochemistry in an effort to elucidate further the differences in electron distribution in syn and anti transition states.

It is obvious from the data in Table I that the isotope effects and Hammett  $\rho$  values for the 2,2-diarylethyltrimethylammonium ion must be weighted averages of the true quantities for syn and anti elimination. Nonetheless, it is worthwhile to examine these results to gain information about relative transition-state structures in the syn and anti pathways.

The primary β-tritium isotope effects in Table II are substantial. While the values are smaller than those observed with 2,2-diphenylethyl-2-*t* tosylate,<sup>4</sup> the corresponding  $k_{\text{H}}/k_{\text{D}}$  values (calculated from the known<sup>10,11</sup> relation between  $k_{\text{H}}/k_{\text{T}}$  and  $k_{\text{H}}/k_{\text{D}}$ ) are larger than those observed with 2-phenylethyl-2,2-*d*<sub>2</sub>-trimethylammonium ion under comparable conditions.<sup>12,13</sup> The true difference is probably still greater, for the 2,2-diphenylethyl results contain no contribution from a secondary isotope effect of the nontransferred deuterium as do the results for the 2-phenylethyl

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**Table III.** Primary  $\alpha$ - $^{12}\text{C}/^{14}\text{C}$  Isotope Effects for E2 Reactions of  $\text{R}_1\text{R}_2\text{CH}^{14}\text{CH}_2\text{NMe}_3^+\text{Br}^-$  with  $\text{OH}^-$  in  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  at 50 °C

$\text{Me}_2\text{SO}$ , mol %	$k_{12\text{C}}/k_{14\text{C}}^a$	
	$\text{R}_1 = \text{R}_2 = \text{Ph}$	$\text{R}_1 = \text{Ph}, \text{R}_2 = \text{H}$
30	$1.0232 \pm 0.0020$	$1.0271 \pm 0.0042$
40	$1.0221 \pm 0.0038$	$1.0290 \pm 0.0032$
50	$1.0222 \pm 0.0003$	$1.0245 \pm 0.0025$

<sup>a</sup> Average of three runs with standard deviation.**Table IV.** Secondary  $\alpha$ - $k_{\text{H}}/k_{\text{T}}$  Values for E2 Reactions of  $\text{R}_1\text{R}_2\text{CHCHT}\text{NMe}_3^+\text{Br}^-$  with  $\text{OH}^-$  in  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  at 50 °C

$\text{Me}_2\text{SO}$ , mol %	$k_{\text{H}}/k_{\text{T}}^a$	
	$\text{R}_1 = \text{R}_2 = \text{Ph}$	$\text{R}_1 = \text{Ph}, \text{R}_2 = \text{H}$
30	$1.0264 \pm 0.0022$	$1.0486 \pm 0.0084$
40	$1.0283 \pm 0.0010$	$1.0497 \pm 0.0024$
50	$1.0358 \pm 0.0035$	$1.0597 \pm 0.0013$

<sup>a</sup> Average of three runs with standard deviations.

system.<sup>14</sup> Furthermore, these data do not show a maximum isotope effect between 30 and 40% dimethyl sulfoxide like that observed with the 2-phenylethyl system.<sup>12,13</sup> Instead,  $k_{\text{H}}/k_{\text{T}}$  is almost constant from 30 to 60% dimethyl sulfoxide and then rises. The maximum, if any, must be at or above 80% dimethyl sulfoxide. At 30, 40, and 50% dimethyl sulfoxide, the temperature dependence of  $k_{\text{H}}/k_{\text{T}}$  was determined over at least a 40–50° range;  $E_{\text{a}}^{\text{T}} - E_{\text{a}}^{\text{H}}$  was 2.04–2.06 kcal mol<sup>-1</sup>, and  $A_{\text{aH}}/A_{\text{aT}}$  was 0.48–0.49. While these results could signify a moderate degree of tunneling,<sup>4</sup> it is not safe to draw conclusions from Arrhenius parameters for the sum of two competing processes.<sup>15</sup>

The magnitude of the observed composite  $k_{\text{H}}/k_{\text{T}}$  suggests that  $k_{\text{H}}/k_{\text{T}}$  is probably substantial for both the syn and anti components. Indeed, if the anti component is assumed to have a  $k_{\text{H}}/k_{\text{T}}$  similar to those calculated<sup>10</sup> from  $k_{\text{H}}/k_{\text{D}}$  values in the 2-phenylethyl series,  $k_{\text{H}}/k_{\text{T}}$  would have to be larger for the syn than for the anti process. The reverse is more likely to be true. The transition state in the 2,2-diphenylethyl series would have a greater extent of hydrogen transfer and more carbanion character than that for the 2-phenylethyl series. Thus, there should be less heavy-atom motion in the reaction coordinate and larger  $k_{\text{H}}/k_{\text{T}}$  values.<sup>13</sup> Even so,  $(k_{\text{H}}/k_{\text{T}})_{\text{anti}}$  would have to be rather large for  $(k_{\text{H}}/k_{\text{T}})_{\text{syn}}$  to be comparable to the small isotope effects ( $k_{\text{H}}/k_{\text{D}} < 2$ ) observed for some syn eliminations from quaternary ammonium salts.<sup>16</sup> For example, if there is 50% syn elimination and  $(k_{\text{H}}/k_{\text{T}})_{\text{syn}} = 2$ , an observed  $k_{\text{H}}/k_{\text{T}}$  of 13 would require  $(k_{\text{H}}/k_{\text{T}})_{\text{anti}} = 24$ , corresponding to  $(k_{\text{H}}/k_{\text{D}})_{\text{anti}} = 9.1$ . Thus,  $(k_{\text{H}}/k_{\text{T}})_{\text{syn}}$  is probably large enough that the transition state for syn elimination cannot be very far from linear nor have the proton very unsymmetrically located between substrate and base.

The primary  $\alpha$ -carbon isotope effects (Table III) are somewhat smaller for the 2,2-diphenylethyl than for the 2-phenylethyl system, and the secondary  $\alpha$ -tritium isotope effects (Table IV) are quite markedly smaller. Both of these trends indicate less carbon–nitrogen cleavage in the transition state for syn elimination than in that for anti. Since both sets of effects in the 2,2-diphenylethyl series are composite, the differences between syn and anti effects may be significantly greater than the differences between the observed effects.

The most reasonable conclusion to draw from the isotope effects taken as a whole is that the syn transition state has less carbon–nitrogen cleavage than the anti, but not a markedly different extent of proton transfer. Such a picture would require more carbanion character for the syn than the anti transition state. A study of substituent effects showed, however, that the Hammett  $\rho$  values for the 2,2-diarylethyl system (Table V) are markedly lower than

**Table V.** Rate Constants and Hammett  $\rho$  Values for E2 Reactions of  $(p\text{-XC}_6\text{H}_4)_2\text{CHCH}_2\text{NMe}_3^+\text{Br}^-$  with  $\text{OH}^-$  in  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$  at 60 °C

$\text{Me}_2\text{SO}$ , mol %	$k^a \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for X				Hammett $\rho^b$
	Cl	H	$\text{CH}_3$	$\text{CH}_3\text{O}$	
30	119	4.13	1.05	0.428	$2.43 \pm 0.26$
40	869	30.6	6.70	2.40	$2.54 \pm 0.21$
50	3895	205	53.1	13.3	$2.40 \pm 0.16$

<sup>a</sup> The average of at least two runs, average deviations 1–4%, except 8% for X = Cl in 50%  $\text{Me}_2\text{SO}$ . <sup>b</sup> The  $\rho$  values are calculated by using  $2\sigma_{\text{p}}$  for the substituent constant.

those observed under the same conditions in the 2-phenylethyl system (3.3–3.5).<sup>12</sup>

It is questionable, however, whether the comparison is meaningful. There may be steric constraints on the ability of both  $\beta$ -aryl groups in the 2,2-diarylethyl system to adopt conformations that afford maximum stabilization of a carbanionic center on the  $\beta$ -carbon. The literature affords evidence that comparison of  $\rho$  values for  $\beta$ -arylethyl and  $\beta,\beta$ -diarylethyl systems may be misleading. For example,  $\rho = 2.43$  and 2.26, respectively, for  $\text{Ar}_2\text{-CHCCl}_3$  and  $\text{Ar}_2\text{CHCHCl}_2$  at 30 °C,<sup>17</sup> both values smaller than the 2.61 for  $\text{ArCH}_2\text{CH}_2\text{Cl}$ <sup>18</sup> under almost the same conditions. Yet it would seem virtually certain that both the additional  $\alpha$ -chlorine(s) and the additional  $\beta$ -aryl would make the first two react via substantially more carbanion-like transition states than that for the third.

## Experimental Section

**Solvents.** Fisher ACS grade dimethyl sulfoxide was stirred over calcium hydride for at least 2 days and distilled. The first 10% was discarded. Distilled water was refluxed with potassium permanganate for 2 h and distilled. Absolute ethanol was refluxed over magnesium turnings for at least 8 h and then distilled. The first 10% was discarded. *n*-Butyl alcohol was refluxed over sodium *n*-butoxide and distilled. The first 10% was discarded.

**(Z)-3-Methyl-2-phenyl-1-bromo-1-butene** was obtained by brominating 3-methyl-2-phenyl-1-butene by the procedure of Davis and Roberts.<sup>19</sup> Chromatography on silica gel using pentane as eluant gave first the *E* isomer contaminated with unreacted starting material and then pure *Z* isomer in 30% yield: MS, *m/e* 224, 226 ( $\text{M}^+$ ), 145 ( $\text{M}^+ - \text{Br}$ );  $^1\text{H}$  NMR  $\delta$  1.04 (d, 6 H), 2.64 (m, 1 H), 6.16 (d,  $J = 1.47$  Hz, 1 H). The stereochemistry was assigned on the assumption that bromine cis to the methinyl proton should deshield it.<sup>20</sup> The methinyl proton in the *E* isomer is at  $\delta$  3.38.

**(Z)-3-Methyl-2-phenyl-1-butene-1-*d*.** (Z)-3-Methyl-2-phenyl-1-bromo-1-butene (0.0038 mol) in 5 mL of anhydrous ether was cooled to –78 °C and 3.6 mL of 1.6 M (0.0058 mol) *tert*-butyllithium in pentane added slowly. The mixture was stirred 30 min at –78 °C, and 0.15 g of 99.8% deuterium oxide was added dropwise with vigorous stirring. The reaction mixture was allowed to warm to room temperature, water was added, and the ether layer was separated. The aqueous layer was extracted once with ether, and the combined ether extracts were dried over magnesium sulfate. Evaporation of the ether left 0.50 g (90%) of (Z)-3-methyl-2-phenyl-1-butene-1-*d*, shown by NMR to be >97% stereochemically pure:  $^1\text{H}$  NMR  $\delta$  1.10 (d, 6 H), 2.79 (m, 1 H), 4.98 (br s, 1 H). The *E* isomer has the vinyl proton at  $\delta$  5.08.

**(RR,SS)-3-Methyl-2-phenyl-1-butanone-1-*d*.** To an ice-cold solution of (Z)-3-methyl-2-phenyl-1-butene-1-*d* (0.0034 mol) in 5 mL of dry tetrahydrofuran (THF) was added slowly with stirring 1.4 mL of 1 M borane–THF complex. Stirring was continued for 3 h at room temperature, and 0.5 mL of water, 2.5 mL of 3 M sodium hydroxide, and 2.5 mL of 30% hydrogen peroxide added. The mixture was stirred for 4 h and extracted with pentane. The extracts were washed with water and dried over magnesium sulfate. Removal of the solvent left 0.34 g (60%) of product which was used in the next step without further purification.

**(RS,SR)-3-Methyl-2-phenyl-1-(butyl-1-*d*)trimethylammonium Bromide.** The alcohol obtained above was converted to the tosylate<sup>21</sup> which

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in turn was treated with an excess of dimethylamine in benzene in a pressure bottle at 100 °C for 86 h. Excess dimethylamine was removed on a rotary evaporator, the benzene solution extracted with 6 N hydrochloric acid, the extract washed with ether and then basified with potassium hydroxide. The product was extracted with ether, the extract dried over potassium carbonate, and the ether removed. The crude *N,N*-dimethyl-3-methyl-2-phenyl-1-butylamine-1-*d*:  $^1\text{H}$  NMR  $\delta$  0.74 (d, 3 H), 0.92 (d, 3 H), 1.8 (m, 1 H), 2.18 (s, 6 H), 2.4–2.6 (m, 2 H). It was treated without further purification with an excess of methyl bromide in dry ether and the mixture stirred overnight. The precipitate was filtered and recrystallized from ethanol-ether to give material of mp 171–172.5 °C. The corresponding unlabeled material had mp 170–171 °C. Anal. Calcd for  $\text{C}_{14}\text{H}_{23}\text{NBr}$ : C, 58.74; H, 8.39. Found C, 58.60; H, 8.46.

(*E*)- $\alpha$ -Methyl- $\beta$ -bromostyrene was brominated in the same manner as 3-methyl-2-phenyl-1-butene (see above). Chromatography on silica gel with pentane as eluant gave first the *E* isomer in 57% yield:  $^1\text{H}$  NMR  $\delta$  2.19 (s, 3 H), 6.30 (br s, 1 H), 7.19 (s, 5 H).

(*E*)- $\alpha$ -Methylstyrene- $\beta$ -*d* was prepared by the same procedure as for (*Z*)-3-methyl-2-phenyl-1-butene-1-*d* in 83% yield, >97% stereochemically pure by NMR;  $^1\text{H}$  NMR  $\delta$  2.12 (s, 3 H), 5.24 (s, 1 H), 7.0–7.3 (m, 5 H).

(*RR,SS*)-2-Phenyl-1-(propyl-1-*d*)trimethylammonium bromide was obtained from (*E*)- $\alpha$ -methylstyrene- $\beta$ -*d* by the same sequence of reactions used to convert (*Z*)-3-methyl-2-phenyl-1-butene-1-*d* to (*RS,SR*)-3-methyl-2-phenyl-1-(butyl-1-*d*)trimethylammonium bromide (see above). The overall yield was 50%, mp 179.5–180 °C. The unlabeled material, prepared in the same way, had mp 178–180 °C. Anal. Calcd for  $\text{C}_{12}\text{H}_{20}\text{NBr}$ : C, 55.81; H, 7.75. Found: C, 56.01; H, 7.94.

(*E*)-2-Methyl-1-bromo-1-hexene was obtained by brominating 2-methyl-1-hexene by the procedure of Wolinsky, Clark, and Thorstenson.<sup>20</sup> Gas chromatography (12-ft column of 30% SF-96 on Chromosorb W) and 400-MHz  $^1\text{H}$  NMR spectroscopy showed that the crude product contained the *E* and *Z* isomers in a ratio of 1.3:1. Distillation on a spinning-band column (Perkin-Elmer Model 251) gave five fractions boiling in the range 83–85 °C (35 mm). The last 30% was shown by GC to contain 93% *E* isomer and was used in the following preparation.  $^1\text{H}$  NMR *E*:  $\delta$  5.86 (vinyl H), 2.08 (allylic  $\text{CH}_2$ , t). *Z*:  $\delta$  5.83 (vinyl H), 2.20 (allylic  $\text{CH}_2$ , t).

(*E*)-2-Methyl-1-hexene-1-*d* was obtained from the corresponding bromide by the procedure used to prepare (*Z*)-3-methyl-2-phenyl-1-butene-1-*d* (see above), bp 89 °C (lit.<sup>22</sup> bp 91.1–91.5 °C). The 400-MHz  $^1\text{H}$  NMR spectrum showed 92% *E* ( $\delta$  4.620) and 8% *Z* ( $\delta$  4.651) isomers.

(*RR,SS*)-2-Methyl-1-(hexyl-1-*d*)trimethylammonium bromide was obtained in an overall yield of 10% from (*E*)-2-methyl-1-hexene-1-*d* by the sequence of reactions used to prepare (*RS,SR*)-3-methyl-2-phenyl-1-(butyl-1-*d*)trimethylammonium bromide (above).

(*E*)-1-Phenyl-1-(*p*-methoxyphenyl)-2-bromoethylene was obtained by bromination of 1-phenyl-1-(*p*-methoxyphenyl)ethylene in carbon tetrachloride.<sup>23</sup> Distillation gave a fraction of bp 145–150 °C (0.5 mm) which  $^1\text{H}$  NMR spectroscopy showed to be a 1:1 mixture of the *E* and *Z* isomers. Repeated recrystallization from ethanol gave 15% of the *E* isomer, mp 81–81.5 °C (lit.<sup>24</sup> mp 82.5 °C).

(*E*)-1-Phenyl-1-(*p*-methoxyphenyl)ethylene-2-*d* was obtained from the corresponding bromide by the procedure used to prepare (*Z*)-3-methyl-2-phenyl-1-butene-1-*d* (see above).  $^1\text{H}$  NMR spectroscopy (400 MHz) showed <6% unlabeled olefin.

(*RR,SS*)-2-Phenyl-2-(*p*-methoxyphenyl)ethyl-1-*d*)trimethylammonium bromide was obtained in 33% overall yield from (*E*)-1-phenyl-1-(*p*-methoxyphenyl)ethylene-1-*d* by the sequence of reactions used to prepare (*RS,SR*)-3-methyl-2-phenyl-1-(butyl-1-*d*)trimethylammonium bromide (see above). The product had mp 209–211 °C.

(*Z*)-1-Hexene-1-*d* was prepared in 50% yield from 1-hexyne-1-*d*<sup>25</sup> (95% isotopically pure by NMR spectroscopy) by the procedure of Brown and Zweifel,<sup>8</sup> bp 64–65 °C (lit.<sup>9</sup> bp 65 °C).

(*E*)-1-Hexene-1-*d* was prepared in 41% yield from 1-hexyne by the procedure of Kabalka, Newton, and Jacobus,<sup>9</sup> bp 60–64 °C (lit.<sup>25</sup> bp 65 °C), 85% isotopically pure by  $^1\text{H}$  NMR spectroscopy.

(*RS,SR*)-1-Hexanol-1,2-*d*<sub>2</sub>. To an ice-cold solution of (*Z*)-1-hexene-1-*d* (0.082 mol) and sodium borodeuteride (0.035 mol) in 150 mL of dry diglyme was added boron trifluoride etherate (0.045 mol) dropwise with vigorous stirring, followed by 4 h stirring at room temperature. The mixture was treated with 35 mL of water, 35 mL of 3 M sodium hydroxide, and 35 mL of 30% hydrogen peroxide, followed by stirring overnight. The product was extracted with ether and the ether solution

dried over magnesium sulfate. The crude product, containing some diglyme, was used directly without further purification.

(*RR,SS*)-1-Hexanol-1,2-*d*<sub>2</sub> was prepared from (*E*)-1-hexene-1-*d* by the same procedure.

(*RR,SS*)-1-(Hexyl-1,2-*d*<sub>2</sub>)trimethylammonium bromide was obtained from (*RS,SR*)-1-hexanol-1,2-*d*<sub>2</sub> by the same sequence of steps used to prepare (*RS,SR*)-3-methyl-2-phenyl-1-(butyl-1-*d*)trimethylammonium bromide (see above). The product was highly hygroscopic and was handled in Schlenk ware under nitrogen and dried under vacuum.

(*RS,SR*)-1-(Hexyl-1,2-*d*<sub>2</sub>)trimethylammonium bromide was prepared in the same way from (*RR,SS*)-1-hexanol-1,2-*d*<sub>2</sub>.

(2,2-Diphenylethyl-2-*t*)trimethylammonium iodide was prepared from 2,2-diphenylethanol-2-*t*<sup>26</sup> by the procedure used to prepare (*RS,SR*)-3-methyl-2-phenyl-1-(butyl-1-*d*)trimethylammonium bromide (see above), except that methyl iodide instead of methyl bromide was used in the last step. The product had mp 245–246.5 °C, molar activity 7.66 mCi mol<sup>-1</sup>.

Phenylacetone-1-<sup>14</sup>C was obtained in 78% yield from benzyl bromide and sodium cyanide-<sup>14</sup>C by the procedure of Friedman and Schechter.<sup>26</sup>

2-Phenylethylamine-1-<sup>14</sup>C was obtained in 85% yield by Nystrom's procedure.<sup>27</sup>

(2-Phenylethyl-1-<sup>14</sup>C)trimethylammonium bromide was obtained by treatment of 2-phenylethylamine-1-<sup>14</sup>C with formic acid and formaldehyde according to the procedure of Icke and Wisegarver,<sup>28</sup> followed by treatment of the product with methyl bromide in the same manner as in the preparation of (*RS,SR*)-3-methyl-2-phenyl-1-(butyl-1-*d*)trimethylammonium bromide (see above). The product had mp 239–241 °C (lit.<sup>29</sup> mp 238–239 °C), molar activity 0.6898 mCi mol<sup>-1</sup>.

Diphenylacetone-1-<sup>14</sup>C was obtained in 30% yield from phenylacetone-1-<sup>14</sup>C (above) by the procedure of Robb and Schultz.<sup>30</sup>

2,2-Diphenylethylamine-1-<sup>14</sup>C was obtained in 92% yield from diphenylacetone-1-<sup>14</sup>C by Nystrom's procedure.<sup>27</sup>

(2,2-Diphenylethyl-1-<sup>14</sup>C)trimethylammonium bromide was obtained in 80% overall yield from 2,2-diphenylethylamine-1-<sup>14</sup>C by the same steps used to prepare (2-phenylethyl-1-<sup>14</sup>C)trimethylammonium bromide (see above). It had mp 182–184 °C. Anal. Calcd for  $\text{C}_{17}\text{H}_{22}\text{NBr}$ : C, 63.75; H, 6.88. Found: C, 63.94; H, 6.55.

2-Phenylethanol-1-*t*. A solution of 0.4 mol of sodium borohydride in 175 mL of diglyme was divided into two equal portions, and to one of them was added 12.5 mCi of tritiated sodium borohydride and then, slowly, 0.4 mol of 2-phenylacetyl chloride. The mixture was heated on a steam bath for 10 min and then the remaining unlabeled sodium borohydride solution added. The mixture was stirred until it cooled to room temperature and then hydrolyzed by cautious addition of 6 M hydrochloric acid. The product was extracted with ether and the extract dried over magnesium sulfate and distilled. 2-Phenylethanol of bp 100–101 °C (9 mm) (lit.<sup>29</sup> bp 110 °C (20 mm)) was obtained in 58% yield, molar activity 1.62 mCi mol<sup>-1</sup>.

(2-Phenylethyl-1-*t*)trimethylammonium bromide was obtained in 64% overall yield from 2-phenylethanol-1-*t* by the same steps used to prepare (*RS,SR*)-3-methyl-2-phenyl-1-(butyl-1-*d*)trimethylammonium bromide (see above). It had mp 238–240 °C (lit.<sup>29</sup> mp 238–239 °C).

2,2-Diphenylethanol-1-*t* was obtained in 61% yield, activity 1.21 mCi mol<sup>-1</sup>, from diphenylacetyl chloride by the procedure used to prepare 2-phenylethanol-1-*t* (see above). It had bp 137–139 °C (0.5 mm) (lit.<sup>31</sup> bp 144–145 °C (1 mm)).

(2,2-Diphenylethyl-1-*t*)trimethylammonium bromide was obtained in 41% overall yield from 2,2-diphenylethanol-1-*t* by the same steps used to prepare (*RS,SR*)-3-methyl-2-phenyl-1-(butyl-1-*d*)trimethylammonium bromide (see above). It had mp 182.5–184.5 °C.

2,2-Bis(*p*-chlorophenyl)ethylamine. Bis(*p*-chlorophenyl)acetic acid was converted to its amide via its acid chloride by standard procedures, and the amide reduced to the amine in 67% yield by the procedure of Zuccarello et al.<sup>32</sup>

2,2-Bis(*p*-chlorophenyl)ethyltrimethylammonium bromide was obtained by the same sequence of steps used to prepare (2-phenylethyl-1-<sup>14</sup>C)-trimethylammonium bromide (see above). It had mp 230–232 °C. Anal. Calcd for  $\text{C}_{17}\text{H}_{20}\text{NCl}_2\text{Br}$ : C, 52.44; H, 5.14. Found: C, 52.61; H, 5.28.

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**2,2-Bis(*p*-methoxyphenyl)ethylamine.** *p*-Anisaldehyde was condensed with diethyl malonate by the procedure of Allen and Spangler<sup>33</sup> to give diethyl-*p*-methoxybenzylmalonate in 94% yield. This was treated with *p*-anisylmagnesium bromide by the procedure of Newman and Flanagan<sup>34</sup> and the crude product saponified and decarboxylated by the procedure of Zuccarello et al.<sup>32</sup> The resulting 3,3-bis(*p*-methoxyphenyl)-propanoic acid was subjected to a Curtius rearrangement by the procedure of Weinstock<sup>35</sup> and the isocyanate hydrolyzed by refluxing with 1 M sodium hydroxide solution for 7 h. The solution was acidified, boiled for 10 min to dissolve solid material, cooled, extracted with ether, and made basic with potassium hydroxide. The amine was extracted with ether, and the extracts were dried over potassium carbonate. Removal of the ether left 65% (from the acid) of 2,2-bis(*p*-methoxyphenyl)-ethylamine: <sup>1</sup>H NMR δ 1.28 (br, 2 H), 3.20 (d, 2 H), 3.76 (2, 6 H), 3.86 (t, 1 H), 6.7–7.2 (dd, 8 H).

**2,2-Bis(*p*-methoxyphenyl)ethyltrimethylammonium bromide** was obtained from the amine by the same sequence of steps used to prepare (2-phenylethyl-1-<sup>14</sup>C)trimethylammonium bromide (see above). It had mp 228.5–230 °C. Anal. Calcd for C<sub>19</sub>H<sub>26</sub>NO<sub>2</sub>Br: C, 60.00; H, 6.84. Found: C, 60.20; H, 6.71.

**2,2-Bis(*p*-tolyl)ethyltrimethylammonium bromide** was obtained by the same sequence of steps used to prepare 2,2-bis(*p*-methoxyphenyl)ethyltrimethylammonium bromide, starting with *p*-tolualdehyde and diethyl malonate. The product had mp 245–247 °C. Anal. Calcd for C<sub>19</sub>H<sub>26</sub>NBr: C, 65.52; H, 7.47; N, 4.02. Found: C, 65.34; H, 7.60; N, 3.96.

**Stereochemistry of Elimination.** The procedure was essentially the same for all three quaternary ammonium salts that possessed *β*-aryl groups. The substrate (ca. 50 mg) was added to 2 mL of base solution (ca. 0.15 M) that had been equilibrated at the desired temperature. The progress of the reaction was monitored by TLC. Ice and water were added to the cooled reaction mixture, the product was extracted with petroleum ether, and the extracts were washed with water and dried over magnesium sulfate. The solvent was removed and the residue examined by <sup>1</sup>H NMR spectroscopy. From 2-phenyl-3-methyl-1-(butyl-1-*d*)trimethylammonium ion, the ratio of *E* to *Z* olefin was determined from the ratio of the vinyl proton signals at δ 5.24 and 4.96, respectively (100 MHz). From 2-phenyl-2-((*p*-methoxyphenyl)ethyl-1-*d*)trimethylammonium ion the ratio of *E* to *Z* olefin was determined from the ratio of the vinyl proton signals at δ 5.38 and 5.33, respectively (400 MHz). Peaks due to unlabeled material were cleanly separated from those due to the labeled olefins, so no correction for the small amount of unlabeled product was required.

The procedure for the 1-(hexyl-1,2-*d*<sub>2</sub>)trimethylammonium and the 2-methyl-1-(hexyl-1-*d*)trimethylammonium ions was to mix 3 mL of 0.5 M base and 1 mL of 0.7 M substrate, both equilibrated to the desired temperature, in a stainless steel ampule which was then capped tightly and the reaction allowed to proceed for 60 h. The mixture was transferred to a 3-neck rb flask at 80 °C and nitrogen bubbled through the solution to carry the product through a condenser and into a trap cooled with dry ice in acetone. The material in the trap was dissolved in chloroform-*d* and the solution washed with 1 M hydrochloric acid. The 400-MHz <sup>1</sup>H NMR spectrum in the vinyl proton region was taken. The terminal vinyl proton peaks of the products from the unlabeled and labeled 1-hexyl derivatives were located as follows: 1-hexene, δ 4.96 (q), 4.95 (q), 4.92 (m), 4.90 (m); (*E*)-1-hexene-1-*d*, δ 5.00 (t), 4.96 (t); (*Z*)-1-hexene-1-*d*, δ 4.93 (t), 4.90 (t); reaction product from the *RR,SS* reactant, δ 4.97 (m), 4.93 (br), 4.90 (br), and a small peak at δ 5.00 that was ca. 5% of the 4.97 peak. The results show the major products to be (*E*)-1-hexene-1,2-*d*<sub>2</sub> and (*Z*)-1-hexene-1-*d* in about a 3:1 ratio, both the products of anti elimination. No more than 5% of the products of syn elimination, (*Z*)-1-hexene-1,2-*d*<sub>2</sub> and (*E*)-1-hexene-1-*d*, could be present. The product from (*RR,SS*)-2-methyl-1-(hexyl-1-*d*)trimethylammonium ion was purified by GLC before its 400-MHz <sup>1</sup>H NMR spectrum was taken. Integration indicated ca. 82% (*E*)-2-methyl-1-hexene-1-*d* (δ 4.62) and 18% of the *Z* isomer (δ 4.65). Since the 2-methyl-1-hexene-1-*d* used to prepare the *RR,SS* starting material was 92% *E* and 8% *Z* (see above), this result indicates ((18 – 8)/(92 – 8))100 = 12% syn elimination.

**Primary Tritium Isotope Effects.** To 10 mL of a thermally equilibrated 0.008 M solution of the substrate was added 0.08 mL of 2 M sodium hydroxide, and the reaction was allowed to proceed at the desired temperature to approximately 60% completion. Two 0.1-mL samples were withdrawn and diluted with absolute ethanol, and the remaining mixture was quenched with 0.16 mL of 1 M hydrochloric acid. The UV absorbance of the ethanol solutions was determined at 253 nm, where  $\epsilon_p$

**Table VI.** Wavelengths and Molar Absorbances for the Products R<sub>1</sub>R<sub>2</sub>C=CH<sub>2</sub> of the Kinetic Runs<sup>a</sup>

R <sub>1</sub>	R <sub>2</sub>	$\lambda_{\max}$ , nm	$\epsilon \times 10^{-4}$
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	242	2.42
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	253	1.037
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	240	1.98
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	249	2.32
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	244 (248) <sup>b</sup>	1.055 (1.007) <sup>b</sup>
C <sub>6</sub> H <sub>5</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH	234 (248) <sup>b</sup>	0.827 (0.550) <sup>b</sup>

<sup>a</sup> In 95% ethanol. Values for 1,1-diarylethylene derivatives were determined from the absorbance observed after known concentrations of the corresponding 2,2-diarylethyltrimethylammonium salts had reacted completely with base. Pure samples of the other olefins were used to prepare solutions for determination of absorbance. <sup>b</sup> These absorbances and wavelengths were used in the kinetic runs rather than the absorbance at  $\lambda_{\max}$ .

is  $1.037 \times 10^4$  ( $p$  = product) and  $\epsilon_s$  is 340 ( $s$  = substrate). The concentration of 2,2-diphenylethylene ( $c_p$ ) was calculated from the absorbance ( $A$ ) by

$$c_p = (A - c_0\epsilon_s) / (\epsilon_p - \epsilon_s)$$

where  $c_0$  is the initial concentration of substrate. A 2-mL aliquot of the acidified reaction mixture was degassed and distilled on a vacuum manifold as previously described.<sup>4</sup> The composition of the distillate was determined by GC using a 6-ft Poropak T column and helium as carrier gas. Three 0.5-g samples of the distillate were counted, each in 15 mL of Ready-Solv HP cocktail (Beckman Instruments). Quench corrections and calculations of the isotope effects were performed as previously described.<sup>4</sup>

**Primary  $\alpha$ -Carbon Isotope Effects.** To a thermally equilibrated solution of ca. 2 g of the <sup>14</sup>C-labeled substrate in 50 mL of the appropriate H<sub>2</sub>O–Me<sub>2</sub>SO mixture was added an insufficiency of base (40–60% of that calculated for complete reaction) in the form of concentrated sodium hydroxide such that the changes in volume and solvent composition were negligible. After 10 half-lives, 0.08-mL aliquots were taken and diluted to 50 mL with absolute ethanol. The UV absorbance at 248 nm (styrene) or 253 nm (1,1-diphenylethylene) was determined and the product concentration calculated as described above. The remainder of the reaction mixture was cooled to 0 °C and treated with 2 equiv of sodium tetraphenylborate in 100 mL of water. The precipitated quaternary ammonium tetraphenylborate was recrystallized at least twice from acetonitrile–dioxane, ground to a fine powder, and dried in vacuo at 100 °C for at least 10 h. Three weighed samples were counted, each in 15 mL of Ready-Solv HP cocktail (Beckman Instruments). Quench correction and calculations of the isotope effects were performed as previously described.<sup>36</sup>

**Secondary  $\alpha$ -Tritium Isotope Effects.** The procedure for running the reactions, isolating the unreacted substrate, and calculating the isotope effect was the same for the  $\alpha$ -triated as for the  $\alpha$ -<sup>14</sup>C substrates (see above).

**Rate Constants.** Substrate solutions were ca. 0.01 M in most cases and base solutions 0.02–0.10 M. The base and substrate solutions were thermally equilibrated in separate arms of a Y-tube, the solutions quickly mixed, and aliquots withdrawn periodically and diluted with 95% ethanol. The olefin concentration was determined from the UV absorbance. Wavelengths and molar absorbances used are listed in Table VI. At least six points were taken per run and fitted by a linear least-squares program to the integrated equation for the pseudo-first- or second-order rate law, depending upon the concentrations used. The reaction of 2,2-bis(*p*-chlorophenyl)ethyltrimethylammonium bromide with sodium hydroxide in 50% Me<sub>2</sub>SO–H<sub>2</sub>O was too fast for this technique and was followed by rapidly mixing thermally equilibrated substrate ( $6 \times 10^{-5}$  M) and base ( $10^{-4}$  M) solutions and observing directly the UV absorbance in the thermostated cell compartment. The temperature was monitored by an iron–constantan thermocouple.

**Registry No.** (*RS,SR*)-(CH<sub>3</sub>)<sub>2</sub>CHCH(C<sub>6</sub>H<sub>5</sub>)CHDNMe<sub>3</sub><sup>+</sup>Br<sup>–</sup>, 85336-51-2; (*RR,SS*)-*p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH(C<sub>6</sub>H<sub>5</sub>)CHDNMe<sub>3</sub><sup>+</sup>Br<sup>–</sup>, 85336-52-3; (*RR,SS*)-C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)CHDNMe<sub>3</sub><sup>+</sup>Br<sup>–</sup>, 85336-53-4; (*RR,SS*)-*n*-C<sub>4</sub>H<sub>9</sub>CH(CH<sub>3</sub>)CHDNMe<sub>3</sub><sup>+</sup>Br<sup>–</sup>, 85336-54-5; (*RR,SS*)-*n*-C<sub>4</sub>H<sub>9</sub>CHDCHDNMe<sub>3</sub><sup>+</sup>Br<sup>–</sup>, 85336-55-6; (*RS,SR*)-*n*-C<sub>4</sub>H<sub>9</sub>CHDCHDNMe<sub>3</sub><sup>+</sup>Br<sup>–</sup>, 85336-56-7; Ph<sub>2</sub>CTCH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>I<sup>–</sup>, 85336-57-8; Ph<sub>2</sub>CH<sup>12</sup>CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Br<sup>–</sup>, 85336-58-9; PhCH<sub>2</sub><sup>12</sup>CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Br<sup>–</sup>, 6068-85-5; Ph<sub>2</sub>CH<sup>14</sup>CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Br<sup>–</sup>, 85336-59-0; PhCH<sub>2</sub><sup>14</sup>CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Br<sup>–</sup>.

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Br<sup>-</sup>, 85336-60-3; Ph<sub>2</sub>CHCH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Br<sup>-</sup>, 85336-61-4; PhCH<sub>2</sub>CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Br<sup>-</sup>, 85336-62-5; (p-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CHCH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Br<sup>-</sup>, 85336-63-6; Ph<sub>2</sub>CHCH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Br<sup>-</sup>, 85336-58-9; (p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CHCH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Br<sup>-</sup>, 85336-64-7; (p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>CHCH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>Br<sup>-</sup>, 85336-65-8; (p-ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C=CH<sub>2</sub>, 2642-81-1; (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>C=CH<sub>2</sub>, 530-48-3; (p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C=CH<sub>2</sub>, 2919-20-2; (p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C=CH<sub>2</sub>, 4356-69-8; CH<sub>3</sub>C(C<sub>6</sub>H<sub>5</sub>)=CH<sub>2</sub>, 98-83-9; (CH<sub>3</sub>)<sub>2</sub>CHC(C<sub>6</sub>H<sub>5</sub>)=CH<sub>2</sub>, 17498-71-4; T, 10028-17-8; <sup>14</sup>C, 14762-75-5; *t*-BuLi, 594-19-4; HNMe<sub>2</sub>, 124-40-3; D, 7782-39-0; (Z)-3-methyl-2-phenyl-1-bromo-1-butene, 85336-66-9; 3-methyl-2-phenyl-1-butene, 17498-71-4; (E)-3-methyl-2-phenyl-1-bromo-1-butene, 85336-67-0; (Z)-3-methyl-2-phenyl-1-butene-*l*-d, 85336-68-1; (RR,SS)-3-methyl-2-phenyl-1-butanol-*l*-d, 85336-69-2; *N,N*-dimethyl-3-methyl-2-phenyl-1-butylamine-*l*-d, 85336-70-5; (E)- $\alpha$ -methyl- $\beta$ -bromostyrene, 16917-35-4; (E)- $\alpha$ -methylstyrene- $\beta$ -d, 69912-51-2; (E)-2-methyl-1-bromo-1-hexene, 85336-71-6; (Z)-2-methyl-1-bromo-1-hexene, 85336-72-7; 2-methyl-1-hexene, 6094-02-6; (E)-2-methyl-1-hexene-*l*-d, 85336-73-8; (Z)-2-methyl-1-hexene-*l*-d, 85336-74-9; (E)-1-phenyl-1-(*p*-methoxyphenyl)-

2-bromoethylene, 5783-23-3; 1-phenyl-1-(*p*-methoxyphenyl)ethylene, 4333-75-9; (Z)-1-phenyl-1-(*p*-methoxyphenyl)-2-bromoethylene, 5556-73-0; (E)-1-phenyl-1-(*p*-methoxyphenyl)ethylene-2-*d*, 85336-75-0; 1-hexyne-*l*-d, 7299-48-1; (Z)-1-hexene-*l*-d, 18963-99-0; (E)-1-hexene-*l*-d, 18963-98-9; 1-hexyne, 693-02-7; (RS,SR)-1-hexanol-*l*,2-*d*<sub>2</sub>, 85336-76-1; (RR,SS)-1-hexanol-*l*,2-*d*<sub>2</sub>, 85336-77-2; phenylacetone-*l*-<sup>14</sup>C, 4701-32-0; benzyl bromide, 100-39-0; sodium cyanide-<sup>14</sup>C, 3396-82-5; 2-phenylethylamine-*l*-<sup>14</sup>C, 85336-78-3; diphenylacetone-*l*-<sup>14</sup>C, 85336-79-4; 2,2-diphenylethylamine-*l*-<sup>14</sup>C, 85336-80-7; 2-phenylethanol-*l*-*t*, 55110-72-0; 2-phenylacetyl chloride, 103-80-0; 2,2-diphenylethanol-*l*-*t*, 85336-81-8; diphenylacetyl chloride, 1871-76-7; 2,2-bis(*p*-chlorophenyl)ethylamine, 85336-82-9; bis(*p*-chlorophenyl)acetic acid, 83-05-6; bis(*p*-chlorophenyl)acetyl chloride, 68668-89-3; bis(*p*-chlorophenyl)-acetamide, 52234-91-0; 2,2-bis(*p*-methoxyphenyl)ethylamine, 85336-83-0; *p*-anisaldehyde, 123-11-5; diethyl malonate, 105-53-3; diethyl *p*-methoxybenzalmalonate, 6768-23-6; *p*-anisyl bromide, 104-92-7; 3,3-bis(*p*-methoxyphenyl)propanoic acid, 35582-69-5; 2,2-bis(*p*-methoxyphenyl)-1-isocyanatoethane, 85336-84-1; *p*-tolualdehyde, 104-87-0.

## Heterogeneous Permanganate Oxidations. 3. Mechanism of the Oxidation of Alcohols by Hydrated Copper Permanganate

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**Abstract:** Secondary alcohols dissolved in methylene chloride are readily oxidized to the corresponding ketones when treated with hydrated permanganate salts under heterogeneous conditions. However, the addition of equimolar amounts of an alkene almost completely inhibits the reaction, apparently by formation of  $\pi$  complexes on the surface of the oxidant. When mixtures of saturated secondary and  $\beta,\gamma$ -unsaturated alcohols are treated with hydrated copper permanganate, the unsaturated alcohols are preferentially oxidized, although the converse is true when each alcohol is oxidized separately. These observations suggest that unsaturated compounds must form organometallic complexes on the reactive sites of the reagent and that oxidation of unsaturated alcohols may be initiated by complexation of the double bond followed by rearrangement within the coordination shell of manganese to give an oxygen complex that can be converted to the corresponding unsaturated ketone. The fact that  $\gamma,\delta$ -unsaturated alcohols are not oxidized under these conditions indicates that, if the hydroxyl is not close to the point at which the  $\pi$  bond forms, it does not interact with the oxidant, possibly because it cannot come into the coordination shell of the manganese(VII) ion.

### Introduction

The use of heterogenous reagents often increases the ease of execution and the selectivity of specific synthetic procedures.<sup>1,2</sup> This is particularly true for oxidation reactions where the use of solid oxidants gives products that are not contaminated with reduced oxidant and which are therefore more easily isolated and purified. For example, the use of solid permanganate salts under a solvent such as methylene chloride gives a product that is not contaminated with manganese dioxide as frequently occurs when the reaction is carried out in aqueous solutions<sup>3,4</sup> or in organic solvents with the aid of phase-transfer agents.<sup>5-8</sup>

Although chromium(VI),<sup>9-12</sup> iron(III),<sup>13</sup> periodate,<sup>14</sup> and hypochlorite<sup>15</sup> have also been used as solid oxidants, the largest number of synthetic applications have come from the use of permanganate in contact with molecular sieves,<sup>16</sup> silica,<sup>16,17</sup> alumina,<sup>18</sup> or hydrated metal cations such as sodium monohydrate<sup>19</sup> or copper(II) pentahydrate.<sup>20-22</sup> The hydrated cation can be introduced either by use of the appropriate permanganate salt (e.g.,

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