Mechanisms of Elimination Reactions. 39. Steric and Electronic Effects on Stereochemistry in Eliminations from Primary Alkyltrimethylammonium Salts[1,2]

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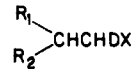
Abstract: Percentages of syn elimination have been determined by high-field NMR on the products of elimination from $R_1R_2CHCHDX$. The results for X = OTs with *t*-BuO^-/*t*-BuOH at 60 °C were the following (R_1, R_2, % syn): *p*-$MeOC_6H$, C_6H_5, 3.7; *p*-ClC_6H_4, C_6H_5, 29; *p*-ClC_6H_5, C_6H_5, 0 in EtO^-/EtOH. For X = NMe_3^+ with OH^- in 50 mol % Me_2SO–50 mol % H_2O at 60 °C, the results were as follows (R_1, R_2, % syn): *p*-$MeOC_6H_4$, C_6H_5, 60; *p*-ClC_6H_4, C_6H_5, 72. For Ar(*i*-Pr)-$CHCHDNMe_3^+$ with OH^- in 50 mol % Me_2SO–50 mol % H_2O at 80 °C, the results were as follows (Ar, % syn): *m*-ClC_6H_4, 78.6; *p*-ClC_6H_4, 69.5; C_6H_5, 59.6; *p*-EtC_6H_4, 58.3; *p*-*t*-BuC_6H_4, 60.5. Overall rates in this series were dissected into syn and anti rates, which fitted the Hammett equation to give $\rho_{syn} = 3.69 \pm 0.20$ and $\rho_{anti} = 3.02 \pm 0.22$. This result supports the conclusion that syn elimination has a more carbanionic transition state than anti. The lower percent syn with X = OTs than with X = NMe_3^+ is ascribed to the lesser steric requirements of OTs.

The stereochemistry of bimolecular elimination reactions has been shown over the past 20 years or so to follow a complex pattern ranging from all anti to all syn, including cases where one stereoisomer is formed by anti and the other by syn elimination.[3,4] Quaternary ammonium salts are particularly prone to syn elimination, but primary alkyltrimethylammonium ions appeared to eliminate exclusively or predominantly anti[5,6] until it was shown that β branching could cause syn elimination to become the major path.[7] The present research was undertaken to explore the role of the leaving group and of substituent effects in syn eliminations from β-branched primary alkyl derivatives.

The substrates used were all of the general formula **1**. They were stereospecifically synthesized by the general procedure described earlier for similar compounds.[7] Base-promoted elimination



1a, R_1 = C_6H_5; R_2 = *p*-ClC_6H_4; X = $NMe_3^+I^-$
b, R_1 = C_6H_5; R_2 = *p*-$MeOC_6H_4$; X = $NMe_3^+I^-$
c, R_1 = C_6H_5; R_2 = *p*-ClC_6H_4; X = OTs
d, R_1 = C_6H_5; R_2 = *p*-$MeOC_6H_4$; X = OTs
e, R_1 = *i*-Pr; R_2 = *m*-ClC_6H_4; X = $NMe_3^+I^-$
f, R_1 = *i*-Pr; R_2 = *p*-ClC_6H_4; X = $NMe_3^+I^-$
g, R_1 = *i*-Pr; R_2 = C_6H_5; X = $NMe_3^+I^-$
h, R_1 = *i*-Pr; R_2 = *p*-EtC_6H_4; X = $NMe_3^+I^-$
i, R_1 = *i*-Pr; R_2 = *p*-*t*-BuC_6H_4; X = $NMe_3^+I^-$

reactions were performed on these substrates and the resulting mixtures of stereoisomeric deuterated olefins analyzed by high-field NMR.[7] The results are recorded in Tables I and II.

Table I demonstrates three points. First, there is less syn elimination with tosylate than with trimethylammonio as leaving group. Correction for the difference in base and solvent for the two leaving groups should, if anything, increase the disparity between the percent syn values, for *tert*-butoxide in *tert*-butyl alcohol is generally more effective in promoting syn elimination than is hydroxide in mixtures of dimethyl sulfoxide and water.[8,9] Second, *tert*-butoxide in *tert*-butyl alcohol gives more syn elimination than ethoxide in ethyl alcohol. The superiority of tertiary over primary alkoxides in promoting syn elimination has been noted before.[3,8] Third, the electron-withdrawing *p*-chloro substituent increases the proportion of syn elimination from both the tosylate and the quaternary ammonium salt (**1a** and **1c**) relative to the corresponding substrates (**1b** and **1d**) with the electron-releasing *p*-methoxy substituent.

Table I. Stereochemistry of Elimination from ArPhCHCHDX at 60 °C

Ar	X	base/solvent[a]	% syn
p-ClC_6H_4	OTs	EtO^-/EtOH	0
p-ClC_6H_4	OTs	*t*-BuO^-/*t*-BuOH	29
p-$MeOC_6H_4$	OTs	*t*-BuO^-/*t*-BuOH	3.7
p-ClC_6H_4	$NMe_3^+I^-$	OH^-/50%Me_2SO-50%H_2O	72
p-$MeOC_6H_4$	$NMe_3^+I^-$	OH^-/50%Me_2SO-50%H_2O	60

[a] Solvent composition in mol %.

Table II. Rates and Stereochemistry of Elimination from (*3*-Methyl-2-(X-phenyl)-1-butyl-*1-d*)trimethylammonium Iodides with Hydroxide Ion in 50% Me_2SO–50% H_2O[a] at 80 °C

X	$k_2 \times 10^5$ M^{-1} s^{-1} [b]	% syn	$k_{syn} \times 10^5$ M^{-1} s^{-1}	$k_{anti} \times 10^5$ M^{-1} s^{-1}
m-Cl	230 ± 10.0	78.6	175	47.7
p-Cl	96.6 ± 0.6	69.5	67.1	29.5
H	11.6 ± 0.02	59.6	6.79	4.61
p-Et	3.14 ± 0.003	58.3	1.83	1.31
p-*t*-Bu	3.08 ± 0.01	60.5	1.86	1.22

[a] Solvent composition in mol %. [b] Each value is the average of at least three determinations with standard deviation.

The effect of the leaving group can be readily understood in terms of our steric explanation of syn elimination from primary substrates.[7] The anti transition state, **2**, should be less stable, the larger R_1, R_2, and X thereby allowing syn elimination to compete more effectively. Trimethylammonio is a poorer leaving group than tosylate, a characteristic which could also promote syn elimination by increasing the carbanion character of the transition state (see below). We believe, however, that the steric difference

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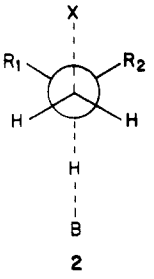

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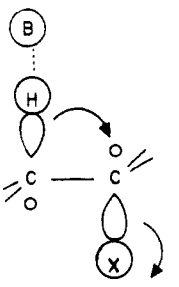
is so great that its effect predominates.

The different results with *p*-chloro and *p*-methoxy substituents indicate that electron withdrawal favors syn elimination. We tried to prepare a wider to of stereospecifically deuterated substrates of the type of **1a–d**, but difficulties in separating the stereoisomeric vinyl bromide precursors caused us to abandon this approach. We turned instead to **1e–i**, where the vinyl bromides could be separated readily by chromatography on silica gel. The overall rates of elimination with hydroxide in 50% dimethyl sulfoxide–50% water at 80 °C were measured, and the stereochemistry of elimination was determined under the same conditions, enabling us to dissect the overall rate into rates of syn and anti elimination. The results are recorded in Table II.

It is qualitatively evident that both anti and syn elimination are facilitated by electron-withdrawing substituents, the latter more so than the former. When the rate constants are fitted to the Hammett equation, the resulting ρ values are 3.50 ± 0.18 for the overall reaction, 3.02 ± 0.22 for the anti elimination, and 3.69 ± 0.20 for the syn elimination. These values at 80 °C may be compared to 2.4 at 60 °C for (2,2-diarylethyl)trimethylammonium ion[7] (probably mixed syn-anti) and 3.4 at 60 °C for (2-arylethyl)trimethylammonium ion[10] (probably all anti[5]). We have previously suggested that the low value for the 2,2-diarylethyl system results from the inability of both aryl groups to attain the conformations necessary to interact effectively with the developing carbanionic center.[7] That ρ_{anti} in the present case is less than ρ for the 2-arylethyl system may reflect a similar restrictive effect of the β-isopropyl group on the conformation of the aryl group.

The most significant comparison is that ρ_{syn} is substantially larger than ρ_{anti}, indicating that the transition state for syn elimination has more carbanion character than the transition state for anti elimination. A similar result is reported for the reaction of 2-arylcyclopentyl tosylates with *tert*-butoxide in *tert*-butyl alcohol at 50 °C, where the trans series (syn elimination) gives a ρ of 2.8 while the cis series (anti elimination) has a ρ of only 1.5.[11] Thus, greater carbanion character for syn than anti elimination seems to be found independent of the nature of the leaving group or the structure of the substrate.

The present results provide additional support for theoretical discussions which have emphasized the role of carbanion character in syn elimination. Ingold originally suggested that the E2 reaction could be viewed as an "S_N2" displacement of the leaving group by the electrons of the β-C–H bond.[12] Normally an anti-periplanar arrangement of the C–H and C–X bonds would be required for a smooth backside displacement (**3**). If the β-C–H bond is nearly broken and a carbanionic center nearly fully formed in the transition state, as in **4**, the lobe of the developing p orbital opposite the C–H bond could contain enough electron density for a "backside" displacement of the leaving group. The overall result would then be a syn-periplanar elimination. This idea has been taken up extended by a number of workers, including Zavada and Sicher,[13,14] Lowe,[15] and Bach.[16]



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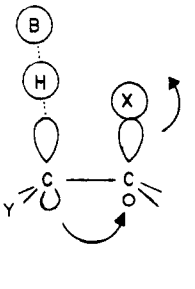

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The molecular orbital approach of Bach[16] has contributed several important insights. One is that the "displacements" in **3** and **4** can be viewed as interaction of the C–H bonding electrons with the vacant σ^* orbital of the C–X bond. In order for this to occur efficiently in **4**, inversion at C_β must precede or accompany C–X bond breaking, implying either an E1cB or an E1cB-like E2 mechanism. The experimental results indicate that the E1cB character need not be extreme, for all of the ρ values are below those found (4–7) in typical carbanion-forming reactions.[17-19]

Experimental Section

Solvents. Ether was refluxed over sodium with benzophenone used as an indicator of dryness.[20] It was then distilled. Dimethyl sulfoxide was stirred over calcium hydride for 2 days. It was distilled under reduced pressure and the first 10% discarded. Distilled water was refluxed over potassium permanganate for 2 h and then distilled. *tert*-Butyl alcohol was stirred over calcium hydride for 24 h and then distilled. The first 10% of distillate was discarded. Absolute ethanol was refluxed over magnesium turnings for 8 h and then distilled. The first 10% of distillate was discarded. Tetrahydrofuran was refluxed over sodium with benzophenone used as an indicator of dryness.[20] It was then distilled.

General. All melting and boiling points are uncorrected. The NMR spectra were recorded on a Bruker WH-400 or a Nicolet QE 300 NMR spectrometer in all cases involving distinctions between or analyses of stereoisomeric olefins and their mixtures. A Varian EM-390 NMR spectrometer was used in some less critical cases. Chloroform-*d* and dimethyl-d_6 sulfoxide were used as NMR solvents. Mass spectra were determined on a VG 7035 mass spectrometer.

(*RS*,*SR*)-2-Phenyl-2-(*p*-methoxyphenyl)ethyl-*1*-*d* tosylate was an intermediate in the synthesis of (*RR*,*SS*)-(2-phenyl-2-(*p*-methoxyphenyl)ethyl-*1*-*d*)trimethylammonium bromide.[7] Recrystallization from ethanol gave material of mp 59.0–62.5 °C: ^{1}H NMR δ 2.48 (s, 3 H), 4.33 (d, 1 H), 4.51 (d, 1 H), 6.8–7.8 (m, 13 H); MS 383 (M^+).

(*RR*,*SS*)-(2-Phenyl-2-(*p*-methoxyphenyl)ethyl-*1*-*d*)trimethylammonium iodide was obtained by the procedure previously used for the corresponding bromide,[7] substituting methyl iodide for methyl bromide. ^{1}H NMR δ 3.01 (s, 9 H), 3.68 (s, 3 H), 4.12 (d, 1 H), 4.59 (d, 1 H), 7.15 (dd, 4 H), 7.28 (m, 5 H).

(*Z*)-1-Phenyl-1-(*p*-chlorophenyl)-2-bromoethylene was obtained by the same method used to prepare (*E*)-1-phenyl-1-(*p*-methoxyphenyl)-2-bromoethylene.[7] The oily crude mixture of *E* and *Z* bromides was refluxed with potassium hydroxide in ethanol to ensure complete elimination from the precursor dibromide. The *Z* isomer crystallized when the mixture was left at room temperature for 48 h. Recrystallization from ethanol gave material of mp 88–89.5 °C (lit.[21] mp 88–89 °C): ^{1}H NMR δ 6.71 (s, 1 H), 7.0–7.6 (m, 9 H).

(*RS*,*SR*)-(2-Phenyl-2-(*p*-chlorophenyl)ethyl-*1*-*d*)trimethylammonium iodide was obtained from (*Z*)-1-phenyl-1-(*p*-chlorophenyl)-2-bromoethylene by the same sequence of reactions used to prepare (*RR*,*SS*)-(2-phenyl-2-(*p*-methoxyphenyl)ethyl-*1*-*d*)trimethylammonium iodide (above and ref 7). It had mp 122–123 °C; ^{1}H NMR δ 3.01 (s, 9 H), 4.20 (d, 1 H), 4.79 (d, 1 H), 7.2–7.5 (m, 5 H), 7.50 (dd, 4 H).

(*RR*,*SS*)-2-Phenyl-2-(*p*-chlorophenyl)ethyl-*1*-*d* tosylate was an intermediate in the synthesis of (*RS*,*SR*)-(2-phenyl-2-(*p*-chlorophenyl)-

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ethyl-*1-d*)trimethylammonium iodide (see above). Recrystallization from ethanol gave material of mp 66.0–66.8 °C; ^{1}H NMR δ 2.48 (s, 3 H), 4.31 (d, 1 H), 4.50 (d, 1 H), 6.8–7.8 (m, 13 H).

***p*-Chloroisobutyrophenone** was obtained by adding isobutyryl chloride (0.42 mol) dropwise to a mixture of aluminum chloride (0.28 mol) and chlorobenzene (1.27 mol). When the evolution of hydrogen chloride ceased, the mixture was poured into ice water and the product extracted with ether. The ether was dried over $MgSO_4$ and removed. The resulting mixture (78% para and 22% ortho by NMR) was fractionally distilled in vacuum to give ortho isomer, bp 60 °C (ca. 0.5 torr), and pure para isomer, bp 87 °C (ca. 0.5 torr), the latter in 60% isolated yield: ^{1}H NMR δ 1.20 (d, 6 H), 3.45 (m, 1 H), 7.60 (dd, 4 H).

***p*-Ethylisobutyrophenone** was obtained from ethylbenzene by the same procedure as for *p*-chloroisobutyrophenone. The product was 62% para, bp 107 °C (ca. 3 torr), and 38% ortho, bp 90 °C (ca. 3 torr). The para isomer had ^{1}H NMR δ 1.13 (t, 3 H), 1.20 (d, 6 H), 2.62 (q, 2 H), 3.46 (m, 1 H), 7.50 (dd, 4 H).

***p*-(*tert*-Butyl)isobutyrophenone** was obtained from *tert*-butylbenzene by the same procedure as for *p*-chloroisobutyrophenone. The product was 95% para, bp 110 °C (ca. 3 torr), and 5% ortho, bp 95 °C (ca. 3 torr). The para isomer had ^{1}H NMR δ 1.19 (d, 6 H), 1.38 (s, 9 H), 3.52 (m, 1 H), 7.69 (dd, 4 H).

***m*-Chloroisobutyrophenone** was obtained by the chlorination of isobutyrophenone according to the procedure of Pearson, Pope, Hargrove, and Stampler for the chlorination of acetophenone.[22] The product, bp 85 °C (ca. 0.5 torr), was obtained in 33% yield: ^{1}H NMR δ 1.25 (s, 6 H), 3.43 (m, 1 H), 7.6 (m, 4 H).

3-Methyl-2-(*p*-chlorophenyl)-1-butene. A mixture of sodium hydride (0.104 mol) and 200 mL of dimethyl sulfoxide was heated at 60 °C until hydrogen evolution ceased (ca. 1 h). A solution of methyltriphenylphosphonium bromide (0.104 mol) in dimethyl sulfoxide was added slowly, the mixture was stirred for 30 min, and 0.052 mol of *p*-chloroisobutyrophenone was added. The mixture was stirred overnight and poured into ice water, and the product was extracted with pentane. After removal of the pentane and distillation, the product was obtained in 96% yield: ^{1}H NNR δ 1.05 (d, 6 H), 2.76 (m, 1 H), 4.98 (s, 1 H), 5.02 (s, 1 H), 7.22 (dd, 4 H).

(*Z*)-3-Methyl-2-(*p*-chlorophenyl)-1-bromo-1-butene. 3-Methyl-2-(*p*-chlorophenyl)-1-butene (0.061 mol) was dissolved in 250 mL of carbon tetrachloride, a solution of bromine (0.061 mol) in 100 mL of carbon tetrachloride was added dropwise, the mixture was stirred for 2 h, and the solvent was removed. The oily residue was refluxed with 0.06 mol of potassium hydroxide in 200 mL of ethanol for 2 h, the mixture was poured into water, and the product was extracted with pentane. Removal of the pentane afforded a mixture of *E* and *Z* isomers which was chromatographed on silica gel with pentane as eluant to give first the *E* and then the *Z* isomer, the latter in 30% yield: ^{1}H NMR δ 1.00 (d, 6 H), 2.68 (m, 1 H), 6.23 (s, 1 H), 7.18 (dd, 4 H).

(*Z*)-3-Methyl-2-(*p*-chlorophenyl)-1-butene-*1-d* was obtained in 96% yield from (*Z*)-3-methyl-2-(*p*-chlorophenyl)-1-bromo-1-butene by the procedure used to prepare (*Z*)-3-methyl-2-phenyl-1-butene-*1-d*.[7]

(*RR*,*SS*)-3-Methyl-2-(*p*-chlorophenyl)-2-butanol-*1-d* was obtained by the procedure used to prepare (*RR*,*SS*)-3-methyl-2-phenyl-1-butanol-*1-d*,[7] except that extraction of the product was done with ether and the extract washed with aqueous ferrous sulfate before drying over magnesium sulfate.

(*RR*,*SS*)-3-Methyl-2-(*p*-chlorophenyl)-2-butyl-*1-d* tosylate was prepared by a standard procedure[23] and used directly in the next step.

(*RS*,*SR*)-(3-Methyl-2-(*p*-chlorophenyl)-1-butyl-1-*d*)trimethylammonium iodide was obtained in 50% yield from (*RR*,*SS*)-3-methyl-2-(*p*-chlorophenyl)-1-butyl-*1-d* tosylate by the procedure used to prepare (*RS*,*SR*)-(3-methyl-2-phenyl-1-butyl-*1-d*)trimethylammonium bromide,[7] except that methyl iodide was used in the final step. The product had mp 216.5–217 °C: ^{1}H NMR δ 3.01 (s, 9 H), 3.68 (s, 3 H), 4.12 (d, 1 H), 4.59 (d, 1 H), 7.15 (dd, 4 H), 7.28 (m, 5 H).

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Table III. ^{1}H NMR Chemical Shifts of the Vinyl Protons in $R_1R_2C{=}CHD$[a]

R_1	R_2	δ(*E*)[b]	δ(*Z*)[b]
C_6H_5	*p*-ClC_6H_4	5.45	5.43
C_5H_5	*p*-$MeOC_6H_4$	5.38	5.33
i-Pr	*m*-ClC_6H_4	5.18	5.00
i-Pr	*p*-ClC_6H_4	5.02	4.98
i-Pr	C_6H_5	5.10	4.98
i-Pr	*p*-EtC_6H_4	5.06	4.92
i-Pr	*p*-*t*-BuC_6H_4	5.05	4.90

[a] Determined in chloroform-*d*. [b] δ(*E*) is the chemical shift of the *E* isomer and δ(*Z*) the chemical shift of the *Z* isomer.

Table IV. Wavelengths and Molar Absorbances of 3-Methyl-2-(X-phenyl)-1-butenes[a]

X	λ_{max}, nm	$\epsilon \times 10^{-3}$
m-Cl	236	3.80
p-Cl	242	7.51
H	235	9.48
p-Et	240	7.68
p-*t*-Bu	239	8.22

[a] In 95% ethanol.

(*RS*,*SR*)-(3-Methyl-2-(*p*-ethylphenyl)-1-butyl-*1-d*)trimethylammonium iodide was obtained by the sequence of reactions used to prepare (*RS*,*SR*)-(3-methyl-2-(*p*-chlorophenyl)-1-butyl-*1-d*)trimethylammonium iodide and had mp 169–171 °C: ^{1}H NMR δ 0.70 (d, 3 H), 0.90 (d, 3 H), 1.17 (t, 3 H), 1.82 (m, 1 H), 2.61 (m, 3 H), 2.95 (s, 9 H), 3.05 (m, 1 H), 3.90 (1 H), 7.25 (dd, 4 H).

(*RS*,*SR*)-(3-Methyl-2-(*p*-(*tert*-butyl)phenyl)-1-butyl-*1-d*)trimethylammonium iodide was obtained by the sequence of reactions used to prepare (*RS*,*SR*)-(3-methyl-2-(*p*-chlorophenyl)-1-butyl-*1-d*)trimethylammonium iodide and had mp 149–150 °C: ^{1}H NMR δ 0.70 (d, 3 H), 0.88 (d, 3 H), 1.28 (s, 9 H), 1.80 (m, 1 H), 2.93 (s, 9 H), 3.03 (m, 1 H), 3.87 (m, 1 H), 7.33 (dd, 4 H).

(*RS*,*SR*)-(3-Methyl-2-phenyl-1-butyl-*1-d*)trimethylammonium iodide was obtained by the sequence of reactions used to prepare (*RS*,*SR*)-(3-methyl-2-(*p*-chlorophenyl)-1-butyl-*1-d*)trimethylammonium iodide and had mp 179–180 °C: ^{1}H NMR δ 0.71 (d, 3 H), 0.91 (d, 3 H), 1.84 (m, 1 H), 2.98 (s, 9 H), 3.09 (m, 1 H), 3.91 (s, 1 H), 7.39 (m, 5 H).

(*RS*,*SR*)-(3-Methyl-2-(*m*-chlorophenyl)-2-butyl-*1-d*)trimethylammonium iodide was obtained by the sequence of reactions used to prepare (*RS*,*SR*)-(3-methyl-2-(*p*-chlorophenyl)-1-butyl-*1-d*)trimethylammonium iodide and had mp 199.5–200 °C: ^{1}H NMR δ 0.70 (d, 3 H), 0.90 (d, 3 H), 1.82 (m, 1 H) 2.95 (s, 9 H), 3.13 (m, 1 H), 3.91 (s, 1 H), 7.43 (m, 4 H).

Stereochemistry of Elimination. The substrate (ca. 15 mg) was dissolved in 2 mL of solvent, heated to the desired temperature, and mixed with 2 mL of base solution at the same temperature. The reaction was followed to completion by TLC, and the reaction mixture was poured into water. The product was extracted with petroleum ether, the solution was dried over magnesium sulfate, and the solvent was evaporated. The 400 or 300 mHz ^{1}H NMR spectrum of the residue was recorded. The vinyl proton NMR absorbances of the $R_1R_2C{=}CHD$ stereoisomers are listed in Table III.

Kinetics of Elimination Reactions of (3-methyl-2-aryl-1-butyl-*1-d*)-trimethylammonium Iodides. The substrate (20 mg) in 2.5 mL of 50% dimethyl sulfoxide–water was brought to 80 °C in a constant-temperature bath and mixed with 2.5 mL of an equilibrated solution of 0.083 M sodium hydroxide in 50% dimethyl sulfoxide–water. Aliquots (0.15 mL) were withdrawn periodically and diluted to 25 mL with 95% ethanol, and the UV absorbance at λ_{max} for the olefinic product (Table IV) was determined. The data were fitted to the second-order rate law for unequal initial concentrations with use of a linear least-squares program. Each rate constant recorded in Table II is the mean of at least three separate determinations. Standard deviations were less than 4% in all cases.