

Mechanisms of Elimination Reactions. XV. The Effect of Base, Solvent, and Structure on Product Ratios in Elimination Reactions of Some Quaternary Ammonium Salts^{1,2}

Irving N. Feit³ and William H. Saunders, Jr.

Contribution from the Department of Chemistry, The University of Rochester, Rochester, New York 14627. Received March 10, 1970

Abstract: The effect of changing from an *n*- to a *sec*- to a *t*-alkoxide-alcohol medium on the products of the E2 reactions of 2- and 3-pentyltrimethylammonium ion, 2-methyl-3-pentyltrimethylammonium ion, and 2,5-dimethyl-3-hexyltrimethylammonium ion has been studied. The reaction of phenoxide bases with two of the salts was also examined. The most important effect of changing the base-solvent system was found to be that of the strength of the base on the transition-state structure. Stronger bases cause an increase in the proportion of the Hofmann rule olefin by increasing the reactant-like nature of the transition state. The effect of the base on the *trans*:*cis* ratios depends on the stereochemistry of the reaction. If the reaction is purely *anti* the change to a stronger base will cause an increase in the proportion of the *cis*-ene. If *syn* elimination competes with *anti* elimination the change to a stronger base will cause an increase in the proportion of *trans*-ene. In the former case the "normal" pattern of an increase in the Hofmann rule product and a decrease in the *trans*:*cis* ratio will be observed. In the latter case, the "abnormal" pattern of an increase in both the Hofmann rule product as well as the *trans*:*cis* ratio will be observed. The occurrence of the "normal" or "abnormal" pattern gives qualitative information about the stereochemistry. The first example of an acyclic quaternary ammonium salt following the Saytzeff rule is described and is attributed to a steric effect. The effect of the alkyl structure on the *trans*:*cis* ratios is shown to follow the predicted trend.

The change from an *n*-alkoxide-*n*-alcohol medium to a *t*-alkoxide-tertiary alcohol medium causes a change toward increasing Hofmann-rule product for E2 reactions of alkyl halides⁴⁻⁷ and tosylates.⁷⁻¹⁰ This change could be caused by the change in the polarity of the solvent, the strength of the base, or the steric requirements of the base. We felt that a better understanding of the factors causing this change in orientation could be gained from a study of the effect of the base-solvent system on E2 reactions of compounds containing a charged leaving group. The solvent effect on these reactions should be the reverse of that on reactions involving uncharged leaving groups.¹¹

We first studied the products from E2 reactions of 2-pentyltrimethylammonium ion under a variety of conditions (Table I). On changing from an *n*-alkoxide-*n*-alcohol medium to a *t*-alkoxide-tertiary alcohol medium there was a small increase in the proportion of 1-pentene, the Hofmann rule product. Control experiments with synthetic olefin mixtures demonstrated that the small differences observed were real.¹² This conclusion is reinforced by the data for reactions in the *sec*-alkoxide-secondary alcohol medium which was intermediate between that of the *n*- and *t*-alkoxide-alcohol systems.

- (1) This work was supported by the National Science Foundation.
- (2) A preliminary report has been published: I. N. Feit and W. H. Saunders, Jr., *Chem. Commun.*, 610 (1967).
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- (12) The data for this and other control experiments discussed below are given in the Thesis of I. N. F.

Suitable control experiments precluded the possibility of olefin rearrangement or fractionation under the reaction conditions or during the work-up.¹² The 2-pentene formed was not due to the presence of 3-pentyltrimethylammonium ion as an impurity in the 2-pentyl salt. Reactions of 2-pentyltrimethylammonium salts made from 2-pentanone which was prepared by the treatment of butyryl chloride with dimethylcadmium gave the same results as did the salts made from commercial 2-pentanone.¹²

Despite these precautions we desired a more conclusive trend. We therefore examined the products from the E2 reactions of 2-methyl-3-pentyltrimethylammonium ion. Here the competition is between removal of a proton on a secondary carbon atom and a proton on a tertiary carbon atom, leading to 4-methyl-2-pentene, the Hofmann rule product, and 2-methyl-2-pentene, the Saytzeff rule product, respectively. We hoped that this competition would be less extreme than the competition between removal of a proton on a primary *vs.* a secondary carbon atom, as occurs in the case of the 2-pentyl salts. The results are given in Table II. The trend toward increasing Hofmann rule product with increasingly branched base-solvent systems is conclusively confirmed. The fact that the same qualitative trend is observed for quaternary ammonium salts, tosylates, and halides on changing the base-solvent system rules out the change in solvent polarity as an important factor.

It is also apparent from Tables I and II that it is not the size of the alkyl chain of the base but the extent of chain branching that is important. There are only minor differences in reactions run in ethyl alcohol, *n*-propyl alcohol, or *n*-butyl alcohol; or in reactions run in isopropyl and *sec*-butyl alcohol. The only exception to this generalization is the small difference in the product proportions between reactions run in allyl

Table I. Orientation Studies of E2 Reactions of 2-Pentyltrimethylammonium Salts in Alcohol Solvents

Alcohol ^a	Temp, °C	Rxn time, hr	% 1-pentene ^{b,c}	<i>trans</i> : <i>cis</i> 2-pentene ^b	% methyl alkyl ether ^{b,d}	% yield ^e
Ethyl	78.5 ^f	13	96.0 ± 0.1	<i>g</i>	<i>g</i>	
Ethyl	110	174	94.0	<i>g</i>	<i>g</i>	63 ^h
<i>n</i> -Propyl	110	12	95.7 ± 0.1	0.32 ± 0.02	21 ± 2	71-81
<i>n</i> -Butyl	110	5	94.6	0.31		66 ^h
Allyl	110	66	93.7	0.36	21	52
<i>sec</i> -Butyl	60	120-144	97.4 ± 0.2	0.28 ± 0.01	16 ± 2	82-87
<i>sec</i> -Butyl	85	12-35	97.0 ± 0.1	0.32 ± 0.02	19.6 ± 0.2	77-80
<i>sec</i> -Butyl	110	24	96.6	0.40		71 ^h
<i>t</i> -Butyl	82.8 ^f	4-44	97.7 ± 0.2	0.41 ± 0.01	6.0 ± 0.3	86-88
<i>t</i> -Butyl	110	5	97.2 ± 0.1	0.42 ± 0.03	6.2 ± 0.9	84

^a The base is the corresponding alkoxide. ^b Average deviation indicated for repeated reactions. ^c 1-Pentene + 2-pentene = 100. ^d Olefin + ether = 100. ^e Total yield of olefin and ether determined by means of an internal standard. ^f Refluxing solvent. ^g The 20-ft 20% adiponitrile column used to analyze the *cis*- and *trans*-2-pentenes in other experiments could not be used because methyl ethyl ether and *trans*-2-pentene were not resolved. The 20-ft 28% didecyl phthalate column used in this case did not resolve the *cis*- and *trans*-2-pentene. ^h Olefin yield only.

Table II. Orientation Studies of E2 Reactions of 2-Methyl-3-pentyltrimethylammonium Salts in Alcohol Solvents

Alcohol ^a	Temp, °C	Rxn time, hr	% 4-methyl-2-pentene ^{b,c}	<i>trans</i> : <i>cis</i> ^b 4-methyl-2-pentene	% methyl alkyl ether ^{b,d}	% yield ^e
Ethyl	110	23-40	61.9 ± 1.7	5.2 ± 0.3		
<i>n</i> -Butyl	117.7 ^f	14-44	62.1 ± 0.6	4.6 ± 0.1	65 ± 1	75-94
<i>n</i> -Butyl	110	32-39	63.8 ± 0.3	4.9 ± 0.1	66 ± 1	48-73
Allyl	110	60-65	58.0 ± 0.8	4.4 ± 0.3	49 ± 3	53-70
Isopropyl	110	15	72.3 ± 0.3	<i>g</i>	61	68
<i>sec</i> -Butyl	60	36-90	74.9 ± 0.3	9.9 ± 0.3	74 ± 1	95-96
<i>sec</i> -Butyl	85	36-60	75.8 ± 0.1	9.2 ± 0.2	71 ± 3	74-90
<i>sec</i> -Butyl	110	21-26	76.5 ± 0.2	9.2 ± 0.2	61 ± 3	90
<i>t</i> -Butyl	82.8 ^f	50-60	85.2 ± 0.3	12.2 ± 0.5	51 ± 1	82-94
<i>t</i> -Butyl	110	7-39	83.6 ± 0.3	11.0 ± 0.9	46 ± 1	85-95

^a The base is the corresponding alkoxide. ^b Average deviation indicated. ^c 4-Methyl-2-pentene + 2-methyl-2-pentene = 100. ^d Olefin + ether = 100. ^e Olefin and ether determined by means of an internal standard. ^f Refluxing solvent. ^g The 20-ft 20% adiponitrile used in this experiment did not separate *cis*- and *trans*-4-methyl-2-pentene. The 40-ft tricresyl phosphate column regularly used to separate the methylpentenes could not be used in this case because the isopropyl methyl ether and *trans*-4-methyl-2-pentene were not resolved.

oxide-allyl alcohol and those run in the other *n*-alkoxide-*n*-alcohols.

Before further discussion of the orientation effects, a brief summary of available information on the nature of the transition state in E2 reactions of quaternary ammonium salts is desirable. First, the β -hydrogen is believed under most conditions to be more than half transferred in the transition state.¹³ The increase in the deuterium isotope effect and the decrease in the Hammett ρ value when the base-solvent pair is changed from ethoxide-ethanol to *t*-butoxide-*t*-butyl alcohol with the 2-arylethyltrimethylammonium ions indicate less β -hydrogen transfer and a more reactant-like transition state in the latter case.¹⁴ This conclusion is reinforced by the observation of a decrease in the nitrogen isotope effect with ethyltrimethylammonium ion upon the same base-solvent change.¹⁵

Since the carbanion character actually decreases in the more branched alkoxide-alcohol medium, the trend toward more Hofmann-rule product clearly cannot be ascribed to an increased sensitivity to the inductive effect of β -alkyl substitution. A decrease in double-bond character of the transition state must constitute at least part of the effect by decreasing the influence of product stability on transition-state energy.

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The trend is also consistent with a steric effect. In the *t*-butoxide-*t*-butyl alcohol reaction the trimethylammonio group is closer to the alkyl chain than it is in the *n*-alkoxide-*n*-alcohol reactions. Also, a *t*-alkoxide is more bulky than an *n*-alkoxide. A steric effect involving the base⁴ or the leaving group¹⁶ or both could explain the observed trend.

A factor which has not been considered so far in the discussion is the stereochemistry of the elimination reaction. Since it has been shown that the tendency toward *syn* elimination increases from *n*-alkoxide-*n*-alcohol to *t*-alkoxide-tertiary alcohol media,¹⁷ at least some of our elimination reactions must have substantial *syn* components. The probable role of *syn* elimination in specific instances, particularly its effect on *trans*:*cis* ratios, is discussed in more detail below. While the occurrence of *syn* elimination may indirectly affect Hofmann-Saytzeff ratios *via* eclipsing effects, there does not seem to be any very pronounced direct effect, judging from the invariance of the 2-hexene:3-hexene ratio from 3-hexyltrimethylammonium ion with changing alkoxide-alcohol.¹⁷

The question of whether double bond character or a steric effect is the more important influence on orientation was approached by studying the effect of chain

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Table IV. Olefin Proportions from E2 Reactions of 2-Methyl-3-pentyltrimethylammonium Bromide with Phenoxide Bases in Alcohol Solvents at 135°

Base	Solvent	4-Methyl-2-pentene, % ^{a,b}	<i>trans</i> : <i>cis</i> ^{a,b}
PhOK	<i>t</i> -BuOH	52 ± 2	6.6 ± 0.2
PhOK	<i>n</i> -BuOH	49 ± 1	6.1 ± 0.1
<i>p</i> -NO ₂ PhOK	<i>n</i> -BuOH	41 ± 1	8.9 ± 0.5

^a Average and average deviation. ^b 4-Methyl-2-pentene + 2-methyl-2-pentene = 100.

Table V. Olefin Proportions from E2 Reactions of 3-Pentyltrimethylammonium Bromide with Alkoxide and Phenoxide Bases in Alcohol Solvents at 135°

Base	Solvent	2-Pentene <i>trans</i> : <i>cis</i> ^a
PhOK	<i>t</i> -BuOH	0.48 ± 0.02
PhOK	<i>n</i> -BuOH	0.48 ± 0.04
<i>p</i> -NO ₂ PhOK	<i>n</i> -BuOH	0.58 ± 0.01
<i>n</i> -BuOK	<i>n</i> -BuOH	0.38 ± 0.01
<i>sec</i> -BuOK	<i>sec</i> -BuOH	0.59 ± 0.02
<i>t</i> -BuOK	<i>t</i> -BuOH	0.88 ± 0.01

^a Average of at least two runs with average deviation.

anti eliminations. Tables IV and V give the olefin distributions for reactions of 2-methyl-3-pentyl- and 3-pentyltrimethylammonium bromide with phenoxide and *p*-nitrophenoxide ion in *n*- and *t*-butyl alcohol. With the 2-methyl-3-pentyl salt the change from *p*-nitrophenoxide ion in *n*-butyl alcohol to phenoxide ion in *n*- or *t*-butyl alcohol caused an increase in the proportion of 4-methyl-2-pentene, the Hofmann rule olefin, but a decrease in the ratio of *trans*:*cis* 4-methyl-2-pentene. The *trans*:*cis* 2-pentene ratio from the E2 reaction of the 3-pentyl salt also decreases on changing to the stronger phenoxide. The expected "normal" trend has obviously been attained with the phenoxide bases.

Tables IV and V illustrate two further aspects of the elimination reactions of quaternary ammonium salts. First, the change of base in the same solvent (compare lines 2 and 3) caused larger changes in orientation than a change of solvent with the same base (compare lines 1 and 2). This agrees with the conclusion reached earlier that the change in solvent is not an important factor in the change in orientation that occurs when the base and solvent are changed simultaneously.

Also from Tables IV and V, the change in orientation caused by the change in the base from *p*-nitrophenoxide to phenoxide shows that a change in the strength of the base is sufficient to affect olefin proportions since the steric requirements of these bases are the same. The same conclusion can be drawn, though more tenuously, from the difference in orientation for reactions run in *n*-alkoxide-*n*-alcohol systems and those run in the allyl oxide-allyl alcohol system (see Tables I and II). This is consistent with the conclusion based on the E2 reactions of 2,5-dimethyl-3-hexyltrimethylammonium bromide (see above) that it is not the change in the steric size of the base that causes the changes in orientation.

The *trans*:*cis* ratios and the factors influencing them merit some further comment. A comparison of Tables I and II shows that the *trans*:*cis* 2-pentene ratio from 2-pentyltrimethylammonium ion is nearly constant at

0.3–0.4, while the ratio of *trans*:*cis* 4-methyl-2-pentene from 2-methyl-3-pentyltrimethylammonium ion ranges from 4 to 12 in different alkoxide-alcohol media. In order to cancel out the influence of simple eclipsing effects, the *trans*:*cis* 2-pentene ratios from 3-pentyltrimethylammonium ion were determined. Table V shows that the ratio varies from 0.37 to 0.88 between *n*-butoxide-*n*-butyl alcohol and *t*-butoxide-*t*-butyl alcohol, in contrast to the near constancy of the ratio from 2-pentyltrimethylammonium ion. It has been shown that the 2-hexyltrimethylammonium → 2-hexene reaction shows less tendency toward *syn* elimination than 3-hexyltrimethylammonium → 2-hexene or 3-hexene.²³ The difference is believed to arise from hindrance of the *anti* → *trans* route by alkyl substitution on a β' position (the β position of the branch into which elimination is not occurring).^{17,23} There is, consequently, more *syn* elimination in the 3-pentyl than in the 2-pentyl system, and the increase in *trans* olefin with the branched alkoxide-alcohol media results from the strong preference for *trans* olefin in *syn* elimination. The variation in *trans*:*cis* 4-methyl-2-pentene from 2-methyl-3-pentyltrimethylammonium ion undoubtedly also arises from the incursion of *syn* elimination. Although a difference in *trans*:*cis* 2-pentene ratios is also found with 2- and 3-pentyl tosylates,¹⁶ the cause may not be precisely the same. With the tosylates, steric interactions of the unsymmetrical leaving group and the alkyl chain are probably important.¹⁰

Experimental Section²⁵

2-Pentylamine was prepared in 70% yield by the Raney nickel²⁶ reduction of 2-pentanone oxime according to the procedure of Iffland and Yen,²⁷ bp 87.5–88.5° (lit.²⁷ bp 88–90°).

2-Pentylidimethylamine was prepared by treatment of 2-pentylamine with formaldehyde and formic acid.²⁸ The product, in 27% yield, had bp 117.5° and *n*_D²⁵ 1.4050.

2-Pentyltrimethylammonium Iodide. 2-Pentylidimethylamine (9.5 g) was quaternized with methyl iodide (14 g) in anhydrous ether overnight at room temperature. The salt obtained in 83% yield after recrystallization from *t*-butyl alcohol, had mp 183–184° dec (lit.¹⁶ mp 180°). *Anal.* Calcd for C₈H₂₀NI: C, 37.36; H, 7.84; N, 5.45. Found: C, 37.18; H, 7.83; N, 5.44.

2-Pentyltrimethylammonium Bromide. A solution of 1.6 g of 2-pentylidimethylamine and 15 g of methyl bromide in anhydrous ether was allowed to stand overnight in a sealed tube. After filtration, the hygroscopic salt was recrystallized from ethanol-ether and dried in an Abderhalden apparatus. The 87% yield of 2-pentylidimethylammonium bromide had mp 227–227.5° dec. *Anal.* Calcd for C₈H₂₀NBr: C, 45.72; H, 9.59; N, 6.67. Found: C, 45.49; H, 9.59; N, 6.64.

2-Pentyltrimethylammonium iodide from synthesized 2-pentanone was prepared in order to exclude unambiguously contamination by the 3-pentyl isomer for comparison with the 2-pentyltrimethylammonium iodide prepared from commercial 2-pentanone. 2-Pentanone was prepared by the action of dimethylcadmium on butyryl chloride.²⁹ The oxime of the synthesized 2-pentanone was converted into 2-pentyltrimethylammonium iodide in the same way as was the oxime of the commercial 2-pentanone (see above). This salt had mp 188–190° dec.

2-Methyl-3-pentanone. Treatment³⁰ of 69 g of isobutyronitrile with ethylmagnesium bromide (3.6 mol) led to a 38% yield of 2-

(25) Melting points and boiling points are uncorrected. Elemental analyses were done by Micro-Tech Laboratories.

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methyl-3-pentanone, bp 113–115°, n_D^{25} 1.3965 (lit.³¹ bp 113.7–114.5°, n_D^{25} 1.3961).

2-Methyl-3-pentylidimethylamine, prepared from 2-methyl-3-pentanone oxime as above, had bp 133.5°, n_D^{25} 1.4175.

2-Methyl-3-pentyltrimethylammonium iodide, prepared in 85% yield by letting a solution of 5 g of 2-methyl-3-pentylidimethylamine and 17 g of methyl iodide in anhydrous ether stand for 2 weeks, had mp 222.5–223.5°. *Anal.* Calcd for $C_9H_{22}NI$: C, 39.86; H, 8.18; N, 5.17. Found: C, 39.79; H, 8.10; N, 5.24.

2-Methyl-3-pentyltrimethylammonium Bromide. 2-Methyl-3-pentylidimethylamine (5 g) and methyl bromide (20 g) were dissolved in 100 ml of dry nitromethane and left standing for 2 days. The reaction mixture was added to anhydrous ether to precipitate the salt. After recrystallization from ethanol-ether, a 75% yield was obtained, mp 244–245° dec. *Anal.* Calcd for $C_9H_{22}NBr$: C, 48.21; H, 9.82; N, 6.25. Found: C, 48.00; H, 9.96; N, 6.17.

2,5-Dimethyl-3-hexanone oxime was more difficult to prepare than the other oximes used in this study. It was necessary to heat 10 g of 2,5-dimethyl-3-hexanone, 7 g of hydroxylamine hydrochloride, and 4 g of sodium hydroxide in 75 ml of water for 48 hr on a steam bath before the carbonyl absorption in the infrared spectrum disappeared. A 48% yield of the oxime was isolated. Under otherwise similar conditions, 2-pentanone oxime and 2-methyl-3-pentanone oxime were formed in essentially quantitative yields in 1 and 20 hr, respectively, at room temperature.³²

2,5-Dimethyl-3-hexylidimethylamine was prepared as above from 2,5-dimethyl-3-hexanone oxime in 42% yield, bp 96–98° (90 mm), n_D^{25} 1.4256. This compound showed only one peak on a 10-ft glpc column of 15% Carbowax 20 M and 4% KOH on Chromosorb P operated at 85° with a 75 cc/min helium flow rate.

2,5-Dimethyl-3-hexyltrimethylammonium bromide was prepared by allowing 1 g of 2,5-dimethyl-3-hexylidimethylamine and 7 g of methyl bromide in 7 ml of 5:2 (by volume) nitromethane-ethanol to stand in a sealed tube for 2 days. The reaction mixture was added to anhydrous ether and the resulting precipitate was treated with charcoal, recrystallized from ethanol-ether, and dried in an Abderhalden apparatus. The product had mp 202–204° dec. *Anal.* Calcd for $C_{11}H_{26}NBr$: C, 52.37; H, 10.39; N, 5.55. Found: C, 52.10; H, 10.36; N, 5.59.

3-Pentylidimethylamine. 3-Pentyl tosylate (10 g) was heated for 67 hr at 85° with dimethylamine (6.8 g) in 50 ml of dry benzene in a sealed tube³³ giving a 45% yield of 3-pentylidimethylamine, bp 115–116° (lit.³⁴ bp 116–117°).

3-Pentyltrimethylammonium bromide was prepared by the treatment of 2 g of 3-pentylidimethylamine with 6 g of methyl bromide in 3 ml of dry tetrahydrofuran for 10 hr at room temperature in a sealed tube. After adding the reaction mixture to anhydrous ether, the precipitate was filtered and dried in an Abderhalden apparatus, giving a 67% yield of 3-pentyltrimethylammonium bromide, mp 234–236° dec. *Anal.* Calcd for $C_8H_{20}NBr$: C, 45.72; H, 9.59; N, 6.67. Found: C, 45.62; H, 9.57; N, 6.67.

Alkyl methyl ethers, for comparison of glpc retention times with those of reaction products, were prepared by treatment of the alkoxide with methyl iodide. The products were dried by repeated distillation from potassium. In each case the infrared spectrum and physical properties were consistent with the expected ether.

Purification of Solvents for Product Studies. *n*-Butyl alcohol was distilled twice from potassium metal under a nitrogen atmosphere. Isopropyl and *sec*-butyl alcohols were distilled twice from sodium metal under a nitrogen atmosphere. *t*-Butyl alcohol was dried by distillation from potassium. Methyl, ethyl, *n*-propyl, and allyl alcohols were refluxed over magnesium turnings and distilled. The water content of the *n*-, *sec*-, and *t*-butyl alcohols purified by the methods described above was shown to be less than 0.05%. The analysis was by glpc on an Aerograph A90-P with a 10 ft \times 0.25 in. column of Porapak-Q (Waters Associates) operated at 200°.

Preparation of Alkoxide Solutions for Product Studies. Potassium or sodium metal was added to the appropriate dry alcohol as described previously.¹⁰ Phenoxide and *p*-nitrophenoxide solutions were prepared by adding a 2:1 excess of phenol or *p*-nitrophenol to an alkoxide-alcohol solution.

Procedure for Product Studies. Alcohol solutions 0.1–0.5 *N* in alkoxide and 0.03–0.1 *N* in the quaternary ammonium salt were refluxed or placed in tightly sealed stainless steel tubes, described by Saunders and Ashe,³⁵ and heated in a constant temperature bath. At the end of the desired time period the reaction mixtures were distilled into a Dry Ice-acetone trap. A known weight of *n*-pentane (Phillips, Pure Grade) was then added and the solution analyzed by glpc.

Glpc Analysis of Reaction Products. The distillates from the reactions were analyzed on an Aerograph A-600 B Hy-Fi. The 2,5-dimethylhexane and pentene mixtures were separated on a 20 ft \times 0.125 in. column of 20% adiponitrile on Chromosorb P at 40 and 30°, respectively. The methylpentene mixture was separated on a 40 ft \times 0.125 in. column of tricresyl phosphate (Burrell Corp.) at 50°.³⁶ The identity of the products was determined by comparing retention times with those of known compounds and by coinjection of known compounds with the reaction mixtures. The areas under the peaks were measured by means of a Disc Integrator. Per cent yields were determined by comparing the areas of the product peaks with that of the *n*-pentane peak and correcting for the molar response coefficients.

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