Mechanisms of Elimination Reactions. XIII. The Effect of Base, Solvent, and Structure on Product Ratios in Elimination Reactions of Some Secondary Tosylates[1]

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Abstract: Olefin proportions have been determined for E2 and E1 reactions of 2-pentyl, 3-pentyl, 2-methyl-3-pentyl, 4-methyl-2-pentyl, 3-methyl-2-butyl, and 3-hexyl tosylates. The E2 reactions were performed with the corresponding potassium alkoxide as base in *n*-butyl alcohol, *sec*-butyl alcohol, and *t*-butyl alcohol. The E1 reactions utilized the same solvents with added 2,6-lutidine to prevent acid-catalyzed decomposition. The proportion of the less-substituted olefin increases in the order *n*-butoxide < *sec*-butoxide < *t*-butoxide in the E2 reactions. The *trans/cis* ratios decrease in the same order, and are below unity with *t*-butoxide for all reactants except 2-methyl-3-pentyl tosylate. The *trans/cis* ratios of the olefins run consistently higher when the reactant is the 3-alkyl rather than the isomeric 2-alkyl tosylate. Product proportions in the E1 reactions are relatively unaffected by change of solvent, except that 2-methyl-3-pentyl and 3-methyl-2-butyl tosylates give increasing amounts of hydrogen shift in the order *n*-BuOH < *sec*-BuOH < *t*-BuOH. Possible explanations of these results are discussed.

An increase in Hofmann-rule product in E2 reactions on changing from ethoxide in ethanol to *t*-butoxide in *t*-butyl alcohol (and other branched alkoxide–alcohol pairs) was first noted by Brown with alkyl bromides.[3] Similar results have more recently been obtained with tosylates[4] and quaternary ammonium salts.[5] With the tosylates, the *t*-butoxide eliminations also possess the intriguing feature of a *trans/cis* ratio less than unity in the 2-olefin produced.[4] Brown explains this effect as arising from greater freedom of motion of the arenesulfonate and *t*-butoxide groups when both alkyl groups are on the same side. Froemsdorf[4b] ascribes the effect more specifically to hindrance of rotation about the sulfur–oxygen bond of the arenesulfonate, which he believes to be more important in the *t*-butoxide eliminations because the carbon–oxygen bond is less stretched than in the ethoxide eliminations.

Independent evidence that arenesulfonate leaving groups can exert a steric effect is found in work of Bartsch and Bunnett[6] on the reaction of 2-hexyl derivatives with methoxide in methanol. A plot of log *k*(1-hexene) *vs.* either log *k*(*trans*-2-hexene) or log *k*(*cis*-2-hexene) is closely linear for the halides, but the brosylate falls below the line. This observation suggests that the halide rates are determined predominantly by a polar effect, but that formation of the 2-hexene from the brosylate is subject to steric retardation.

We felt that a more thorough investigation of a range of alkyl tosylates should provide a better understanding of the roles of steric and electronic effects in determining the Hofmann–Saytzev and *trans–cis* ratios. Rather than compare ethoxide–ethanol with *t*-butoxide–*t*-butyl alcohol, we chose the isomeric series *n*-butoxide–*n*-butyl alcohol, *sec*-butoxide–*sec*-butyl alcohol and *t*-butoxide–*t*-butyl alcohol. Effects arising simply from changes in solvent polarity should be minimized in this series for the size (though not the shape) of the hydrocarbon portion of the molecule remains the same.

Our product proportions are recorded in Tables I–IV. With two of the compounds, 2-methyl-3-pentyl and 3-methyl-2-butyl tosylates, the occurrence of some E1 reaction under E2 conditions was indicated by the presence of products of hydrogen shift from the tertiary β-carbon, 2-methyl-1-pentene, and 2-methyl-1-butene, respectively. The olefin proportions in Tables II and III are corrected for the E1 contribution by the method of Colter and McKelvey, using the data in Table V.[7] The maximum contribution of the E1 reaction at the lowest base concentrations was 21–22%. The absence of significant E1 contributions in the E2 reactions of 2-pentyl, 3-pentyl, 4-methyl-2-pentyl, and 3-hexyl tosylates was shown by the invariance of olefin proportions with changes in base concentration. The much lower olefin yields and slower rates in the E1 than in the E2 reactions of these compounds also support this conclusion.

As expected from previous results,[4] the percentage of the less-substituted (Hofmann rule) olefin increases in the order *n*-butoxide < *sec*-butoxide < *t*-butoxide. These increases demonstrate that the extent of chain branching of the alcohol–alkoxide pair is the major factor. Chain branching clearly increases the steric requirements of the base, but even our choice of a series of isomeric alkoxide–alcohol pairs cannot exclude the possibility that at least some of the observed effects arise from changes in base strength or solvent polarity. The use of *n*-butyl alcohol rather than the more common ethanol as our primary alcohol should not complicate comparisons with the literature, for the orientation effects with 2- and 3-pentyl tosylates and *n*-butoxide/*n*-butyl alcohol in Table I are very similar to those reported[4] for the same reactants and ethoxide–ethanol.

The dependence of the Hofmann–Saytzev ratio on the nature of the β-alkyl group is interesting. Comparison of 1-pentene from 2-pentyl (Table I) to 4-methyl-1-pentene from 4-methyl-2-pentyl (Table II) reveals

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(1) This work was supported by the National Science Foundation.

(2) Chas. Pfizer Fellow, 1967–1968.

(3) H. C. Brown, I. Moritani, and Y. Okamoto, *J. Am. Chem. Soc.*, 78, 2193 (1956).

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(6) R. A. Bartsch and J. F. Bunnett, *J. Am. Chem. Soc.*, **90**, 408 (1968).

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Table I. Product Proportions from Elimination Reactions of Pentyl Tosylates with Potassium Alkoxides in the Corresponding Alcohols at 60°

R in ROH	Tosylate	Reaction condn^a	1-Pentene, %^{b,e}	*trans-/cis*-2-Pentene^b	Olefin yield, %^{f}
n-Bu	2-Pentyl	E2	48.9 ± 2.0	1.76 ± 0.02	25.8
s-Bu	2-Pentyl	E2	63.8 ± 1.2	0.78 ± 0.12	35.2
t-Bu^c	2-Pentyl	E2	79.2 ± 1.7	0.31 ± 0.02	45.0
n-Bu	2-Pentyl	E1	11.2 ± 1.2	2.14 ± 0.16	5.8
s-Bu	2-Pentyl	E1	11.4	2.38	6.5
t-Bu	2-Pentyl	E1	9.9	2.14	3.9
n-Bu	3-Pentyl	E2		2.25 ± 0.15	44.9
s-Bu	3-Pentyl	E2		0.99 ± 0.09	46.0
t-Bu^d	3-Pentyl	E2		0.39 ± 0.01	43.6
n-Bu	3-Pentyl	E1		3.26	9.8
s-Bu	3-Pentyl	E1		3.18	11.9
t-Bu	3-Pentyl	E1		2.81	9.9

[a] See Experimental Section for details. [b] Where a range is quoted, result is average of two to four runs. Where no range is quoted, the result is from a single reaction. [c] Reference 4 gives 74.4% 1-pentene, 0.445 *trans-/cis*-2-pentene, conditions unspecified. [d] Reference 4 gives *trans-/cis*-2-pentene of 0.540, conditions unspecified. [e] Relative to total olefin as 100%. [f] Relative to starting material consumed, as determined by an internal standard.

Table II. Product Proportions from Elimination Reactions of Methylpentyl Tosylates with Potassium Alkoxides in the Corresponding Alcohols at 60°

R in ROH	4-Methyl-1-pentene, %^{b,f}	4-Methyl-2-pentene, %^{b,f}	2-Methyl-1-pentene, %^{f}	*trans-/cis*-4-Methyl-2-pentene^b	Olefin yield, %^{g}
4-Methyl-2-pentyl tosylate, E2^a					
n-Bu	55.7 ± 0.3	44.3 ± 0.3	0.0	2.88 ± 0.07	57.7
s-Bu	77.9 ± 3.3	22.1 ± 3.3	0.0	0.88 ± 0.20	62.8
t-Bu	94.3 ± 0.1	5.7 ± 0.1	0.0	0.50 ± 0.14	59.4
4-Methyl-2-pentyl tosylate, E1^a					
n-Bu	11.5 ± 2.2	88.5 ± 2.2	0.0	4.52 ± 0.27	11.8
s-Bu	14.1	85.9	0.0	3.27	11.3
t-Bu	14.0	86.0	0.0	3.54	8.0
2-Methyl-3-pentyl tosylate, E2^a					
n-Bu		31.9 ± 0.5^e	0.0^e	7.43 ± 0.06^e	71.9
s-Bu		42.9 ± 0.5^e	0.0^e	3.03 ± 0.49^e	63.3
t-Bu^c		52.8 ± 2.5^e	0.0^e	1.77 ± 0.22^e	67.0
2-Methyl-3-pentyl tosylate, E1^a					
n-Bu		11.1	9.0	>15	39.0
s-Bu		8.9	15.7	15.4	38.7
t-Bu^d		9.0	19.0	15.0	56.5

[a,b] See corresponding footnotes, Table I. [c] Reference 7 gives 48.9% 4-methyl-2-pentene, *trans–cis* ratio 2.00 at 50°. [d] Reference 7 gives 7.0% 4-methyl-2-pentene (all *trans*), 15.8% 2-methyl-1-pentene at 50°. [e] After correction for an E1 component by the method of ref 7. See Experimental Section and Table V. [f] See Table I, footnote *e*. [g] Relative to starting material consumed, as determined by an internal standard.

Table III. Product Proportions from Elimination Reactions of 3-Methyl-2-butyl Tosylate with Potassium Alkoxides in the Corresponding Alcohols at 60°

R in ROH	Reaction condn^a	3-Methyl-1-butene, %^{b,d}	2-Methyl-1-butene, %^{b,d}	Olefin yield, %^{e}
n-Bu	E2	25.5 ± 1.4^c	0.0^c	46.7
s-Bu	E2	47.4 ± 0.4^c	0.0^c	45.0
t-Bu	E2	76.9 ± 0.9^c	0.0^c	48.7
n-Bu	E1	1.1	7.2	33.0
s-Bu	E1	1.0	11.2	32.9
t-Bu	E1	0.70	15.4	28.5

[a] See Table I, footnote *a*. [b] See Table I, footnote *b*. [c] See Table II, footnote *e*. [d] See Table I, footnote *e*. [e] Relative to starting material consumed, as determined by an internal standard.

Table IV. Product Proportions from Elimination Reactions of 3-Hexyl Tosylate with Potassium Alkoxides in the Corresponding Alcohols at 60°

R in ROH	Reaction condn^a	2-Hexene, %^{b,c}	*trans-/cis*-2-Hexene^b	*trans-/cis*-3-Hexene^b
s-Bu	E2	68.4 ± 0.2	0.76 ± 0.06	0.72 ± 0.33
t-Bu	E2	74.6	0.35	0.36
s-Bu	E1	54.8	2.07	2.61

[a] See Table I, footnote *a*. [b] See Table I, footnote *b*. [c] See Table I, footnote *d*.

that a β-isopropyl is considerably more effective than a β-ethyl at discouraging elimination into the group bearing it. It is also more effective than *two* β-methyls, as shown by 3-methyl-1-butene from 3-methyl-2-butyl (Table III). This is not the order expected from the inductive effects of the alkyl groups, and provides support for Brown's[3] theory of steric hindrance to proton abstraction. The support is not entirely unambiguous, for one could argue that the alkyl groups should exert a stabilizing effect on the developing double bond in the order dimethyl > ethyl > isopropyl, and that the observed order results from competition of this effect with the inductive effect. Evidence for this explanation is found in the preference for elimination into a branch

Table V. Sample Data Used in Correcting Product Proportions in E2 Reactions of 2-Methyl-3-pentyl Tosylate for E1 Component[a]

Base (concn, *M*)	*cis*-4-Methyl-2-pentene, %	*trans*-4-Methyl-2-pentene, %	2-Methyl-2-pentene, %	2-Methyl-1-pentene, %
n-BuOH[b]		11.1	79.8	9.0
n-BuO⁻ (0.26)	2.93	24.4	70.7	1.87
n-BuO⁻ (0.56)	3.30	25.6	69.9	1.16
n-BuO⁻ (1.2)	3.62	27.6	68.2	0.62
t-BuOH[b]	0.6	8.4	72.0	19.0
t-BuO⁻ (0.22)	14.1	30.1	53.2	2.6
t-BuO⁻ (0.34)	16.7	31.4	50.1	1.8
t-BuO⁻ (0.94)	22.6	32.7	44.2	0.5

[a] See Experimental Section for reaction conditions. [b] Solvolysis in the presence of 2,6-lutidine.

bearing two β-methyl groups (compared to a branch bearing one) with *n*-butoxide and *sec*-butoxide on 2-methyl-3-pentyl tosylate (Table II). Finally, the results on 3-hexyl tosylate with *s*-butoxide and *t*-butoxide (Table IV) show a distinct preference for elimination toward the ethyl group over the *n*-propyl group; surprisingly, the preference is about the same as that for elimination toward methyl over *n*-propyl from 2-pentyl tosylate (Table I).

Our *trans/cis* ratios, like those of Brown[4a] and Froemsdorf,[4b] decrease with increasing branching of the alkoxide base, becoming less than unity in many instances. The transition state is expected to resemble reactant more closely with the stronger bases[4b,5] so a part of the decrease is undoubtedly simply a decrease in eclipsing of the α- and β-alkyl groups. The fact that the *trans–cis* ratio goes well below unity requires an additional factor, which is probably a steric effect. Several mechanisms have been suggested for this steric effect.[4,5] We wish to propose a modified steric explanation, but first we must consider the possible role of *syn* elimination.

Incursion of a *syn* mechanism of elimination seems unlikely to be a significant factor in the *trans/cis* ratios. A *syn* mechanism accounts for only 10% of the over-all reaction (16% of *trans* olefin) in the reaction of 5-decyl tosylate with *t*-butoxide in *t*-butyl alcohol.[8] The contribution should be even less with the less-branched alcohol–alkoxide pairs.[9] If *syn* elimination were a controlling factor the *trans/cis* ratio should change in the opposite direction, for *syn* eliminations strongly favor *trans* over *cis* olefin.[10]

The steric mechanism which we have proposed to account for *syn* eliminations with quaternary ammonium salts[9] may play a role in the low *trans/cis* ratios from the tosylates. According to this explanation,[9] the leaving group causes the α- and β-alkyl groups to adopt conformations which shield the *anti*-β-hydrogen. This shielding is more effective in the conformation leading to *trans* than to *cis* olefin. The tosylate is not so bulky a leaving group as trimethylammonio, and the transition state is probably less reactant like, so the rate of formation of *trans* olefin by the *anti* mechanism is not depressed sufficiently for the *syn-trans* pathway to become important. It could easily make the *anti-trans* slower than the *anti-cis* pathway, however.

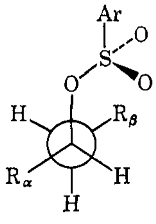
A particularly intriguing aspect of our results is the difference in *trans–cis* ratios of the same olefin from two isomeric reactants. Thus, 3-pentyl tosylate yields consistently more *trans*-2-pentene than does 2-pentyl tosylate (Table I), and the same holds true for the 4-methyl-2-pentene from 2-methyl-3-pentyl and 4-methyl-2-pentyl tosylates (Table II). The regularity of this phenomenon is shown in Table VI, where the ratios of *trans/cis* ratios from the 3-alkyl and 2-alkyl tosylates are given. With one possible exception, these are the same within experimental error for all three solvent-base pairs and any given alkene product In fact, there is very little difference in these ratios between E1 and E2 conditions for the same reactant pairs.

Table VI. Ratios of *trans/cis* Ratios for 2-Enes from Pentyl and Methylpentyl Tosylates

R in ROH	Tosylates	Reaction condn[a]	(*trans-/cis*-3)/(*trans-/cis*-2)[b]
n-Bu	Pentyl	E2	1.28
s-Bu	Pentyl	E2	1.26
t-Bu	Pentyl	E2	1.27
n-Bu	Pentyl	E1	1.52
s-Bu	Pentyl	E1	1.33
t-Bu	Pentyl	E1	1.31
n-Bu	Methylpentyl	E2	2.54
s-Bu	Methylpentyl	E2	3.46
t-Bu	Methylpentyl	E2	3.54
n-Bu	Methylpentyl	E1	~4
s-Bu	Methylpentyl	E1	4.66
t-Bu	Methylpentyl	E1	4.23

[a] See Table I, footnote *a*. [b] Ratio of *trans/cis* olefins from 3-pentyl or 2-methyl-3-pentyl tosylate divided by ratio *trans/cis* olefins from 2-pentyl or 4-methyl-2-pentyl tosylate.

This greater preference for *trans* olefin when the larger group is on the α-carbon and the smaller group on the β-carbon makes it clear that some factor (or factors) other than a simple eclipsing effect is involved. The examination of models reveals several possible steric effects. I and II depict what are probably the most favorable conformations leading to *trans* and *cis* products, respectively. If the arylsulfonyl group is always *anti* to R_α as shown, it can interact sterically with R_β in I, thereby favoring II and lowering the *trans/cis* ratio. This explanation ascribes a common origin to



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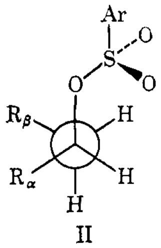

II

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(9) D. S. Bailey and W. H. Saunders, Jr., *ibid.*, 1598 (1968).

(10) J. Sicher, J. Závada, and M. Pánková, *ibid.*, 1147 (1968).

the difference in *trans/cis* ratios from isomeric reactants and to the occurrence of *trans/cis* ratios below unity. The steric bulk of R_β is considered to be the controlling factor, and the bulk of R_α only serves to keep the arylsulfonyl group *anti* to itself.

Another hypothesis utilizes a modified eclipsing effect. When R_α is ethyl or larger, its freedom of rotation will be restricted by the large tosyl group on the same carbon. Thus, it cannot easily rotate so as to minimize eclipsing interactions with R_β. When R_α and R_β are interchanged so that the larger group is R_β, it will have more freedom of rotation than at R_α and eclipsing interactions will be smaller.

Both of the above explanations have the defect of ascribing an indispensable role to the tosyl group. The phenomenon persists, however, in E1 reactions, where the leaving group is usually assumed to depart before the β-proton is lost. This dilemma could be resolved if the elimination occurs from a carbonium–tosylate ion pair in which the tosylate is still close enough to exert a steric effect, or if the carbonium ion loses the β-proton faster than it undergoes conformational change. Evidence for ion pairs in solvolyses of secondary tosylates has been presented,[11] and Skell and Hall[12] argued that the gegenion was involved in the elimination step of E1 reactions because *threo*- and *erythro*-2-butyl-3-*d* tosylates gave different product mixtures.

In comparing the E1 and E2 reactions, one should keep in mind that their stereochemistry may be different. Solvolyses of 1,1,4,4-tetramethyl-7-cyclodecyl tosylate produce olefins primarily by *syn* elimination.[13] An open-chain system more typical of those in the present study, 2-butyl tosylate, gives at least some *syn* elimination in all four solvents studied, and mainly *syn* elimination in two of them, nitrobenzene and acetic acid.[12]

An interesting sidelight of the E1 reactions is that the olefins resulting from hydride shift with 2-methyl-3-pentyl and 3-methyl-2-butyl tosylates, 2-methyl-1-pentene, and 2-methyl-1-butene, respectively, are found in increasing amounts along the solvent series *n*-BuOH < *s*-BuOH < *t*-BuOH. This is in agreement with the work of Lee on 3-methyl-2-butyl tosylate, where hydrogen shift is greater in acetic than formic acid.[14] Evidence for decreased driving force from hydrogen participation in the more polar solvent is afforded by the more recent studies of Closson on solvolyses 2-phenylcyclohexyl tosylates.[15] An obvious and attractive rationale is that the tendency to rearrange to a more stable cation is less in the better ion-solvating solvents. On the other hand, there are clear instances of greater carbon participation the more highly ionizing the solvent.[16] This trend can be rationalized by the assumption that the opportunity for rearrangement is greater in the less nucleophilic solvents. Why opposite trends are followed in hydrogen and carbon participation is not clear. Perhaps nucleophilic solvation of the more exposed hydrogen aids its migration.

Experimental Section[17]

Preparation of Tosylates. The tosylates were prepared in the usual fashion[18] by treating the alcohol with freshly recrystallized *p*-toluenesulfonyl chloride in dry pyridine and leaving the reaction mixture overnight in the refrigerator. The solid tosylates were recrystallized from hexane. The oils were purified by treatment with charcoal followed by washing with petroleum ether at low temperatures (Dry Ice–acetone); yields were 70–80%: **2-pentyl tosylate,** n^{20}D 1.4995 (lit.[19] n^{20}D 1.5001); **3-pentyl tosylate,** mp 42–44° (lit.[20] mp 43.2–44°); **4-methyl-2-pentyl tosylate,** mp 33–35° (*Anal.* Calcd for $C_{13}H_{20}O_3S$: C, 60.89; H, 7.88; S, 12.51. Found: C, 61.09; H, 7.93; S, 12.78); **2-methyl-3-pentyl tosylate,** mp 23–24°, n^{20}D 1.4998 (*Anal.* Calcd for $C_{13}H_{20}O_3S$: C, 60.89; H, 7.88; S, 12.51. Found: C, 61.12; H, 7.91; S, 12.73); **3-methyl-2-butyl tosylate,** n^{25}D 1.4995, mp 18–21° (lit.[21] mp 20.1–20.8°).

Solvent Purification. *n*-Butyl alcohol was distilled under nitrogen from barium oxide. *s*-Butyl alcohol was distilled twice under nitrogen after treatment with sodium metal. *t*-Butyl alcohol was distilled twice after treatment with potassium metal. Analysis by glpc on a column of Poropak Q (Waters Associates) at 200° showed that all alcohols contained <0.05% of water. Water content was checked before use of a batch of solvent.

Preparation of Base Solutions. Potassium metal was scraped clean and washed twice in the appropriate dry alcohol. It was then quickly transferred to the desired volume of dry alcohol under nitrogen. *n*-Butyl alcohol was first cooled in Dry Ice–acetone and allowed to warm to room temperature after addition of potassium; the other alcohols were treated with potassium at room temperature.

Procedure for E2 Reactions. The tosylate (0.05–0.07 g) was weighed directly into a volumetric flask and the flask closed with a serum cap. The base solution (5 ml, 0.2–1.2 *M*) was added by syringe, giving a final tosylate concentration of 0.04–0.06 *M*. The flasks were placed in a constant-temperature bath at 60° until the tosylate had completely reacted. The disappearance of tosylate was monitored in selected cases by tlc on silica gel G with benzene solvent. The plates were developed with iodine. Reaction times ran up to 25 hr in *n*-butyl alcohol, and 35 hr in *s*- and *t*-butyl alcohols.

Procedure for E1 Reactions. The procedure was essentially the same as for the E2 reactions except that the solutions were made up to be 0.04–0.07 *M* in tosylate and 0.18 *M* in 2,6-lutidine (to prevent acid-catalyzed decomposition).[22] Reaction times were 100–150 hr at 60°.

Analysis of Reaction Mixtures. The reaction mixtures were distilled to dryness into a Dry Ice–acetone trap. The distillates were analyzed by glpc on Aerograph Model 600 or Model A-90P instruments. The pentenes were analyzed on a 20 ft × 1/8 in. column of adiponitrile on Chromosorb P at 35°, the methylpentenes and methylbutenes on a 40 ft × 1/8 in. column of tri-*o*-cresyl phosphate[7] at 55°, and the hexenes at room temperature on a column of 20 ft × 0.25 in. adiponitrile followed by a 1.5 ft × 0.25 in. column of silver nitrate in ethylene glycol. Absolute yields were obtained by adding a known weight of pure *n*-pentane to the distilled reaction mixture. The calculated yields are corrected for relative instrument response.

Correction for E1 Component in E2 Reactions. Two of the compounds used in this research gave measurable amounts of olefins derived from carbonium ion rearrangement. They were 2-methyl-3-pentyl tosylate (rearranged product 2-methyl-1-pentene) and 3-methyl-2-butyl tosylate (rearranged product 2-methyl-1-butene). Comparison of the yields of these products in E1 and "E2" reactions enabled calculation of the contribution of the E1 reaction to the reaction run under E2 conditions. The E1 product proportions were then subtracted from the E2 product proportions by the method

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(16) See, for example, S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlessinger, *ibid.*, **74**, 1140 (1952).

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(22) A referee asks whether the 2,6-lutidine could be functioning as a base to cause an E2 contribution. The rearrangements observed with the 2-methyl-3-pentyl and 3-methyl-2-butyl tosylates would not, of course, be observed in a reaction which was largely E2. In addition, R. A. Bartsch, Ph.D. Thesis, Brown University, 1967, p 59, reports an Arrhenius plot for the methanolysis of 2-hexyl brosylate in the presence of 2,6-lutidine. The plot was linear in spite of a twofold variation in the 2,6-lutidine concentration.

of Colter and McKelvey.[7] The method assumes that the E1 product proportions are the same in both the presence and absence of strong base. Two or three base concentrations in the range 0.26–1.2 *M* were used in deriving each figure. The greatest contribution of the E1 reaction to the total elimination product was 21–22% at the lowest base concentrations. Sample data used in calculating the corrections are given in Table VI.

Control Experiments. The absence of a significant E1 component in the reactions of most of the tosylates was shown by runs at two or more base concentrations in the range 0.2–1.2 *M*. Only 2-methyl-3-pentyl and 3-methyl-2-butyl tosylates (see above) showed a regular trend that exceeded experimental error. Synthetic mixtures of the olefins were neither fractionated nor isomerized on exposure to reaction conditions more stringent than those employed on the tosylates, followed by work-up using the procedure described above (conditions: 0.4–0.6 *M* *t*-butoxide in *t*-butyl alcohol at 80° for 20 hr on the pentenes, and 110° for 76 hr on the methylpentenes). While longer reaction times in the E1 reactions sometimes led to decreases in overall yields, olefin proportions were independent of reaction time.

Mechanism and Kinetics of Radiolytically Initiated Cyclohexyl Radical Addition to *cis*- and *trans*-1,2-Dichloroethylene and of the Subsequent Chlorine Atom Elimination Reaction

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Abstract: The kinetics of γ-radiation induced formation of *cis*- and *trans*-1-cyclohexyl-2-chloroethylene by a free-radical chain mechanism in binary solutions of *cis*- and *trans*-1,2-dichloroethylene in cyclohexane was studied at 150°. The condensation reaction between the solvent and the two solutes resulted in the formation of equal ratios of *cis*- and *trans*-c-$C_6H_{11}CH{=}CClH$. The condensation reaction was found to proceed *via* addition of cyclohexyl radicals to the olefins followed by subsequent elimination of a chlorine atom from the intermediate radical. The rate constants for the addition of cyclohexyl radicals to *cis*- and *trans*-1,2-dichloroethylene are estimated at $3.1 \pm 0.4 \times 10^4$ and $9.7 \pm 0.7 \times 10^4$ M^{-1} sec^{-1}, respectively. The rate constants of the chlorine elimination reaction are estimated at $8.6 \pm 2.6 \times 10^3$ and $1.12 \pm 0.37 \times 10^4$ sec^{-1} for the radicals obtained from solutions of *cis* and *trans* isomers, respectively. The possible mechanisms of the addition and elimination reactions are discussed.

The free-radical interaction of olefins and saturated compounds has been the subject of numerous investigations. The interaction of geometrical isomeric olefins with saturated compounds is of particular interest since the steric structure of the products resulting from both isomers may possibly yield valuable information on the mechanism of such reactions.

In recently published work[1] we reported the occurrence of γ-radiation induced free-radical chain condensation reactions of alkanes (RH) with tetrachloroethylene and trichloroethylene. γ irradiation was found to offer some significant advantages in the kinetic study of such reactions. The condensation reactions were found to proceed *via* addition of R radicals to the chloroolefins followed by subsequent elimination of a chlorine atom. We thought it worthwhile to extend this study to solutions of *cis*- and *trans*-1,2-dichloroethylene in alkanes, expecting that in addition to the determination of rate constants for the addition and elimination steps the comparison of the reactivities of the two isomers and their product distributions might yield additional information on the mechanism of such reactions. Cyclohexane was chosen as the alkane solvent since it forms predominantly cyclohexyl radicals upon radiolysis, thus eliminating complications arising from the possibility of different alkyl radicals attaching themselves to the olefins.

Experimental Section

Materials. *cis*- and *trans*-1,2-dichloroethylene (Fluka purum) were purified by distillation. Phillips Research Grade cyclohexane, stated purity 99.99%, was used as received after it was found that treatment with sulfuric acid[2a] did not affect the yield of products, within the experimental error.

Procedure. The sample preparation and irradiation techniques were similar to those used by us previously.[2] The irradiations were carried out in Pyrex ampoules containing 2-ml solutions. The total volume of the ampoules was less than 3 ml. The irradiations were carried out at a dose rate of 2.02×10^{17} eV ml^{-1} min^{-1}. The total dose administered to the *cis*- and *trans*-dichloroethylene solutions was 1.26×10^{18} and 6.28×10^{17} eV ml^{-1}, respectively. The liquid products were determined by gas chromatography (F & M Model 810). The cyclohexylchloroethylenes were analyzed with a 12-ft 20% Ucon on Diatoport column at 150°. The same column at 50° was used for the determination of *cis*-$C_2Cl_2H_2$. *trans*-$C_2Cl_2H_2$ was analyzed with a 16-ft 20% silicon oil DC 200 on Diatoport column at 50°. c-$C_6H_{11}CHCClH$ was identified by mass spectrometric analysis and combustion analysis.

Anal. Calcd for C_8ClH_{13}: C, 66.4; Cl, 24.5; H, 9.1. Found: C, 66.2; Cl, 24.8; H, 8.9.

Nmr and ir techniques were used to differentiate between the *cis* and *trans* isomers of c-$C_6H_{11}CHCClH$. HCl was determined coulometrically.[2b]

Results and Discussion

The main products of the radiolysis of solutions of *cis*- and *trans*-1,2-dichloroethylene are HCl and *cis*- and *trans*-1-cyclohexyl-2-chloroethylene. The yields

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