to the planar structure of the pyridine bases, permitting the reduction of the steric strain by careful orientation of base. It is probable that much larger effects would be observed with highly hindered aliphatic amines, as well as by certain dialkylanilines. Unfortunately, time did not permit the testing of this prediction and we are no longer pursuing this line of investigation.

On the basis of their respective molecular dimensions the steric requirements of ethoxide ion would be expected to be smaller than those of pyridine. However, the results clearly show that ethoxide produces a higher yield of the 1-olefin than does pyridine. It is possible that this anomaly is the result of the strong solvation of the ion, so that ethoxide ion, with its sheath of solvating molecules of ethanol, possesses larger steric requirements than the simple pyridine molecule.

Both with the alkoxide bases and with the pyridine bases there is observed with increasing steric requirements of the base a regular trend from Saytzeff- toward Hofmann-type elimination. The results support the conclusion that both hyperconjugative and steric factors must play a role in controlling the direction of the elimination reaction in simple alkyl halides.

Experimental Part

Materials.—The preparation and physical properties of the alkyl bromides have been described previously.[7]

The pyridine bases were the best available commercial products (Reilly) and were refluxed for 3–4 hours over calcium hydride and then distilled through a column: 2-picoline, b.p. 127° at 751 mm., $n^{20}\text{D}$ 1.5006; 4-picoline, b.p. 141.5° at 742 mm., $n^{20}\text{D}$ 1.5040; 2,6-lutidine, b.p. 142° at 740 mm., $n^{20}\text{D}$ 1.4978.

Procedure for the Elimination Reaction.—In a 200-ml. round-bottomed flask there was placed 100 ml. of 4-picoline and 15.10 g. (0.100 mole) of *t*-amyl bromide. The reaction mixture was attached to a Todd micro column and rapidly heated to reflux. Olefin was removed at the top of the column as rapidly as it appeared there. The product, washed with water, weighed 6.46 g., a yield of 93%. The refractive index, $n^{20}\text{D}$ 1.3850, indicated a composition of 25% 2-methyl-1-butene and 75% 2-methyl-2-butene.

The experiment was repeated with the tertiary bromide being added to the 4-picoline at constant temperature at 70, 100 and 130° and maintained at these temperatures until the elimination reaction was complete. No significant difference in results was realized.

It was shown that synthetic mixtures of olefins could be added to solutions of the hydrobromide in the pyridine bases, maintained at the reflux temperature for several hours, and then recovered in 90–95% yield with no measurable change in composition.

The experimental results are summarized in Table II.

LAFAYETTE, INDIANA

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[7] H. C. Brown and M. Nakagawa, THIS JOURNAL, **77**, 3610 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Elimination Reactions. IX. The Effect of the Steric Requirements of the Leaving Group on the Direction of Bimolecular Elimination in 2-Pentyl Derivatives

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The role of the steric requirements of the leaving group upon the direction of bimolecular elimination has been studied by examining the nature of the products formed in the reaction of potassium ethoxide with a number of 2-pentyl derivatives. 2-Bromopentane yielded 31% of 1-pentene, while 2-pentyl tosylate yielded 48%. The amount of 1-olefin increased to 87% for 2-pentyldimethylsulfonium iodide, increased further to 89% for 2-pentylmethylsulfone, and rose to 98% for 2-pentyltrimethylammonium iodide. It is concluded that these increases in yield of 1-pentene cannot be correlated in terms of the polar properties of the leaving groups. However, the increases can be correlated with their steric requirements. It is concluded that the Hofmann-type elimination exhibited by 'onium salts must be attributed not to the positive charge carried by the 'onium group but attributed instead to the large steric requirements of the group undergoing elimination.

Consideration of the proposed model for the transition state in bimolecular elimination[2] leads to the conclusion that the preferred formation of the most highly alkylated olefin (Saytzeff rule) will be modified by steric effects. It was concluded that an increase in the steric interactions in the transition state by an increase in the steric requirements of the alkyl groups on the incipient double bond, an increase in the steric requirements of the attacking base or an increase in the steric requirements of the leaving group should result in a decreased tendency for the formation of the most highly alkylated olefin and an increased tendency for the formation of the least alkylated olefin (Hofmann rule).[3]

In previous papers we have tested the first two of these conclusions.[2,4,5] In the present paper the effect of the steric requirements of the leaving group upon the direction of the bimolecular elimination reaction is examined in the 2-pentyl system.[6]

In this investigation we examined the structure of the olefins formed in the reaction of potassium ethoxide with 2-pentyl bromide, 2-pentyl iodide, 2-pentyl tosylate, 2-pentyldimethylsulfonium iodide, 2-pentyl methyl sulfone and 2-pentyltrimethylammonium iodide.

Results

2-Bromopentane was synthesized from 2-pentanol by treatment of the tosylate with lithium bro-

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[1] Post-doctorate Fellow at Purdue University, 1953–1954, on a grant provided by the Upjohn Co.

[2] H. C. Brown, I. Moritani and M. Nakagawa, THIS JOURNAL, **78**, 2190 (1956).

[3] An alternative interpretation of the factors controlling the direction of elimination reactions has been proposed; M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

[4] H. C. Brown, I. Moritani and Y. Okamoto, THIS JOURNAL, **78**, 2193 (1955).

[5] H. C. Brown and M. Nakagawa, *ibid.*, **78**, 2197 (1956).

[6] The 2-butyl system is the simplest of those available for such a study. The greater difficulty in handling a gaseous product, 1- and 2-butenes, led us to adopt the 2-pentyl system for this study.

mide in acetone.[7] Treatment with 1 *M* potassium ethoxide in refluxing ethanol gave a 74% yield of pentenes. Infrared analysis indicated the presence of 31% 1-pentene, 18% *cis*-2- and 51% *trans*-2-pentene.

2-Iodopentane was also synthesized from 2-pentanol *via* the tosylate. Its dehydrohalogenation with potassium ethoxide gave very similar results: 74% yield of pentenes analyzing for 30% 1-, 16% *cis*-2- and 54% *trans*-2.

Treatment of the tosylate in this way resulted in a 50% yield of the pentenes. The infrared analysis indicated the composition to be 48% 1-, 18% *cis*-2- and 34% *trans*-2-.

2-Pentylmethyl sulfide was synthesized from 2-pentyl iodide and sodium methyl mercaptide. The sulfide was converted into 2-pentyldimethylsulfonium iodide by treatment with methyl iodide in acetonitrile solution. The isolation of the desired isomeric pentenes from the product formed in the reaction of potassium ethoxide and 2-pentyldimethylsulfonium iodide offered difficulties. Both dimethyl sulfide and methyl ethyl ether possess volatilities so close to that of the pentenes as to render unsatisfactory the separation by distillation. After considerable experimentation it proved possible to achieve the essentially quantitative removal of dimethyl sulfide in the form of its stable complex with mercuric sulfide and the removal of methyl ethyl ether by repeated (30-fold) washing with cold water (0°). In this way the reaction of 2-pentyldimethylsulfonium iodide with potassium ethoxide produced 66% dimethyl sulfide and 60% pentenes. Analysis of the pentenes indicated the presence of 87% 1-, 5% *cis*-2- and 8% *trans*-2-.

2-Pentylmethyl sulfide, prepared as described above, was converted into the sulfone by oxidation with hydrogen peroxide in acetic acid. The reaction with 1 *M* potassium ethoxide proved relatively slow. In other instances no measurable difference in isomer distribution has been observed in utilizing 4 *M* potassium ethoxide in place of the usual 1 *M* base.[4] Accordingly we utilized 4 *M* potassium ethoxide and a somewhat higher temperature (130°) in order to achieve a convenient rate of reaction.[8] There was obtained a 40% yield of pentenes. The product analyzed for 89% 1-, 2.5% *cis*-2- and 9% *trans*-2-.

Treatment of 2-pentyl iodide with trimethylamine in methanol gave largely trimethylamine hydroiodide, presumably arising from the methanolysis of the secondary iodide. However, in acetonitrile trimethylamine reacted satisfactorily with the iodide to form 2-pentyltrimethylammonium iodide. Reaction with 4 *M* potassium ethoxide resulted in a 63% yield of pentene. Analysis indicated the presence of 98% 1-, with approximately 1% each of *cis*- and *trans*-2-.

It is unfortunate that we were unable to utilize identical reaction conditions for the entire series. However, a consideration of the results suggests that no complication has been introduced by the use of a higher reaction temperature in the last two cases. The higher the temperature the lower should be the selectivity of a given reaction. Consequently, the yields of 89 and 98% of 1-pentene, realized in the elimination of 2-pentylmethylsulfone and 2-pentyltrimethylammonium ion, must represent lower limits for the isomer distribution which should result from an elimination reaction carried out at 80°. An increase in the yields of 1-olefin to some higher values in these two cases would not alter the conclusion that in eliminations of 2-pentyl derivatives the yield of 1-olefin increases in the order: $-\mathrm{Br} \sim -\mathrm{I} < -\mathrm{OSO_2Tol} < -\mathrm{SMe_2}^+ < -\mathrm{SO_2Me} < -\mathrm{NMe_3}^+$.

The experimental data are summarized in Table I.

TABLE I

COMPOSITION OF OLEFINS FORMED IN THE REACTION OF POTASSIUM ETHOXIDE WITH 2-PENTYL DERIVATIVES

2-Pentyl derivative, RX	–X	Olefin composition, % 1-	*cis*-2-	*trans*-2-
Bromide[a,c]	–Br	31	18	51
Iodide[a]	–I	30	16	54
Tosylate[a]	$-\mathrm{OSO_2Tol}$	48	18	34
Dimethylsulfonium[a]	$-\mathrm{S(CH_3)_2}^+$	87	5	8
Methyl sulfone[b]	$-\mathrm{SO_2CH_3}$	89	2.5	9
Trimethylammonium[b]	$-\mathrm{N(CH_3)_3}^+$	98	1	1

[a] 1 *M* Potassium ethoxide, 80°. [b] 4 *M* Potassium ethoxide, 130°. [c] H. J. Lucas, T. P. Simpson and J. M. Carter, THIS JOURNAL, **47**, 1462 (1925), report 29% 1-olefin.

Discussion

It is unfortunate that at the present time there are no direct measurements of the different steric requirements of the groups under investigation. It is therefore necessary to utilize the available data on the atomic dimensions and the molecular geometry[9] in order to estimate the relative magnitudes of the steric requirements of the different groups.

The groups utilized in the present may be subdivided into four classes depending upon the presence of none, one, two or three branches on the atom which is directly bonded to the 2-pentyl group. It is reasonable to expect that the steric requirements will increase with the number of such branches.

No branches: –Br, –I
One branch: $-\mathrm{OSO_2Tol}$
Two branches: $-\mathrm{SMe_2}^+$
Three branches: $-\mathrm{SO_2Me}$, $-\mathrm{NMe_3}^+$

The van der Waals radius of iodine is slightly larger than that of bromine, leading to the conclusion that its steric requirements should be somewhat larger. On the other hand, the covalent radius of iodine is also larger than that of bromine which should tend to reduce the difference between the two. We may therefore conclude that the difference in the steric requirements of these two groups will be quite small.

Similarly the larger covalent radius of sulfur as compared to nitrogen suggests that the steric requirements of the methyl sulfone group should be less than those of the trimethylammonium group. This deduction is further supported by the smaller

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[7] A similar procedure was utilized to minimize the possibility for rearrangement; H. Pines, A. Rudin and V. N. Ipatieff, THIS JOURNAL, **74**, 4063 (1952).

[8] The elimination reactions of unsymmetrical sulfones to give olefins and sulfinic acids have been studied previously; C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 708 (1930).

[9] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

steric requirements of the two oxygen atoms in the methyl sulfone group as contrasted with those of the corresponding methyl groups in the trimethylammonium group (van der Waals radii are 1.40 and 2.0 Å for oxygen and methyl, respectively).

Finally, in comparing the methyl sulfone with the dimethylsulfonium group we can balance out the linking sulfur atom in the two groups as well as the common methyl group. We are then left with a comparison of the relative steric requirements of two oxygen atoms as compared to one methyl group. Consideration of molecular models strongly suggests that the steric requirements of the two oxygen atoms should be the greater.

On the basis of such arguments the conclusion is reached that the steric requirements of the groups examined in the present study may be expected to increase in the order: $-\mathrm{Br} < -\mathrm{I} < -\mathrm{OSO_2Tol} < -\mathrm{SMe_2}^+ < -\mathrm{SO_2Me} < -\mathrm{NMe_3}^+$.

These results support the conclusion that the steric requirements of the leaving group must represent an important factor in controlling the direction of elimination in the 2-pentyl system. Consequently, it may be concluded that the proposal that the preferential formation of the least branched olefin in eliminations of 'onium salts (Hofmann rule) is due to the positive charge on the group undergoing elimination[3] is less satisfactory than the proposal that the controlling factor is the large steric requirements of the 'onium group.[10]

Originally it was our intention to study this question further by synthesizing 2-pentylneopentyldimethylammonium iodide. According to the steric interpretation that we favor, the larger steric requirements of the group undergoing elimination in this compound should result in an increased yield of 1-pentene over that obtained in the corresponding reaction of the parent compound. However, our observation that the elimination of 2-pentyltrimethylammonium iodide proceeds almost quantitatively (98%) to the formation of 1-pentene made it impractical to utilize this approach. In any event, the achievement of predominantly Hofmann-type elimination in the case of the methyl sulfone group provides an even stronger argument in favor of the proposed steric basis for eliminations which proceed in accordance with the Hofmann rule.

In these eliminations *trans*-2-pentene is formed in larger amounts than *cis*-2-pentene.[11] The favored formation of the *trans* isomer would be anticipated on the basis of the relative magnitudes of the steric interactions in the two transition states leading to the two isomeric 2-olefins. Since a thorough discussion of this point is now available, further consideration at this time is unnecessary.[12]

Experimental Part

Materials.—A large stock of 2-pentanol (b.p. 118° at 745 mm., n^{20}D 1.4062) was prepared from the reaction of acetaldehyde with *n*-propylmagnesium bromide (65% yield) and the reaction of butyraldehyde with methylmagnesium iodide (70% yield). The alcohol was converted into the tosylate (n^{20}D 1.5001) in 60% yield by Tipson's procedure.[13]

2-Iodopentane was synthesized by the addition of 46.5 g. of 2-pentyl tosylate to a warm saturated solution of 80 g. of sodium iodide in 200 ml. of acetone. Within 10 min. sodium tosylate had precipitated. After 1 hour, water was added, and the oily layer was separated and dried. Fractionation yielded 24.0 g. of the iodide (64% yield), b.p. 139–142°, n^{20}D 1.4948. Infrared examination indicated the absence of the 3-isomer. On the other hand, treatment of 2-pentanol with red phosphorus and iodine gave an iodide whose spectrum indicated the presence of 35% of 3-iodopentane.[7]

2-Bromopentane was synthesized by mixing 50 g. of 2-pentyl tosylate with 40 g. of anhydrous lithium bromide in 300 ml. of acetone.

After 3 days at room temperature, half of the acetone was distilled off under reduced pressure, water was added, and the bromide was taken up in ether. Distillation yielded 13.7 g. of the bromide (40% yield), b.p. 117.5° at 740 mm., n^{20}D 1.4400.

2-Pentylmethyl sulfide was prepared from the iodide, prepared as described above, and sodium methylmercaptide. Methylmercaptan was passed into a solution of 10 g. of sodium (10% excess) in 200 ml. of dry ethanol until the theoretical amount (20.5 g.) had been absorbed. To this solution there was added 78.0 g. of 2-pentyl iodide in 100 ml. of alcohol over a period of 2 hr. while heating under reflux. The cooled reaction mixture was diluted with water, the oil separated with petroleum ether, dried and distilled. There was obtained 30.7 g. (66% yield) of the sulfide, b.p. 63–64° at 60 mm., n^{20}D 1.4468. *Anal.* Calcd. for $C_6H_{14}S$: C, 60.9; H, 11.9. Found: C, 60.3; H, 12.4.

2-Pentylmethyl sulfone was prepared by adding 25 ml. of 30% hydrogen peroxide (30% excess) in portions to a hot solution of 10.1 g. of 2-pentylmethyl sulfide in 20 ml. of acetic acid. When the initial exothermic reaction had ceased, the solution was heated on the steam-bath for 1 hr. The cooled solution was poured into dilute acid and the oil separated with chloroform. Distillation yielded 12.8 g. of the sulfone (86%) as a colorless, mobile oil, b.p. 101–102° at 2 mm., n^{20}D 1.4602. *Anal.* Calcd. for $C_6H_{14}SO_2$: C, 48.0; H, 9.4. Found: C, 48.6; H, 9.6.

2-Pentyldimethylsulfonium iodide was synthesized by treating 10.8 g. of 2-pentylmethylsulfide with 8.7 g. (20% excess) of methyl iodide in 20 ml. of acetonitrile. After 1 day at room temperature, ether was added to precipitate the product. After recrystallization from acetone–ether, the product was obtained in the form of needles, m.p. 118°, in a yield of 17.8 g. (98%). *Anal.* Calcd. for $C_7H_{17}SI$: I^-, 48.78. Found: I^-, 48.48.

2-Pentyltrimethylammonium iodide was obtained by treating 15.0 g. of 2-iodopentane with anhydrous trimethylamine (30 ml., 5 molar excess) and 10 ml. of acetonitrile. After 6 days at room temperature, the tube was opened and 19.5 g. (89% yield) of the product was obtained in the form of micro needles, m.p. 180°, after recrystallization from acetone–ether. *Anal.* Calcd. for $C_8H_{20}NI$: C, 37.4; H, 7.8; N, 5.5; I, 49.4. Found: C, 37.3; H, 8.0; N, 5.3; I, 49.2.

Analysis.—Both infrared and refractive index measurements were utilized in the estimation of 1-pentene. Only the infrared procedure was used for the determination of the *cis/trans* composition.

In utilizing refractive index measurements we took advantage of the fact that the refractive index value for 1-pentene (n^{20}D 1.3714) is considerably lower than the values for the *trans*-2-pentene (n^{20}D 1.3793) and the *cis*-2-pentene (n^{20}D 1.3830)[14] and assumed that the 2-pentenes would be present in essentially their equilibrium distribution at 75° (70% *trans*-2-pentene and 30% *cis*-2-pentene)[15] so that the n^{20}D value for the 2-pentene mixture would be 1.3804.

The infrared determination of 1-pentene was based on peaks at 6.05, 10.05 and 11.0 μ. The low peak at 5.6 μ gave an additional check on these values. For the estimation of *cis*-2-pentene the peaks at 7.65 and 14.36 μ were

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[10] C. H. Schramm, *Science*, **112**, 367 (1950). It should be mentioned that it is our opinion that the transition state utilized by Schramm in his argument is not a feasible one. This point is discussed in the following paper.

[11] In view of these results the statement that the 2-butene obtained in the reaction of potassium ethoxide on 2-bromobutane consists almost entirely of the *cis*-compound is puzzling; M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2058 (1948).

[12] D. Y. Curtin, *Record Chem. Prog.*, **12**, 111 (1954).

[13] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[14] "Selected Values of Properties of Hydrocarbons," American Petroleum Research Projects 44 and 45.

[15] J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

TABLE II

SUMMARY OF EXPERIMENTAL DATA ON THE YIELD AND COMPOSITION OF OLEFINS FORMED IN THE REACTION OF POTASSIUM ETHOXIDE WITH 2-PENTYL DERIVATIVES

2-Pentyl derivative, $CH_3CH_2CH_2\underset{\underset{X}{\vert}}{C}HCH_3$			Olefin, yield		Olefin composition, %			
	g.	mole	g.	%	$n^{20}D$	1-	*cis*-2-	*trans*-2
Bromide[a]	7.00	0.0446	2.20	73	1.3778	28		
	7.00	.0446	2.25	75	1.3779	28		
					(1.3776)[c]	31	18	51
Iodide[a]	10.7	.0543	2.79	74	1.3779	27		
					(1.3776)[c]	30	16	54
Tosylate[a]	12.0	.0494	1.60	50	1.3761	47		
					(1.3763)[c]	48	18	34
Dimethylsulfonium[a]	10.0	.0385	4.48	60	1.3728	85		
	10.0	.0385	1.23	50	1.3727	86		
					(1.3726)[c]	87	5	8
2-Pentylmethyl sulfone[b]	7.7	.0513	1.40	39	1.3723	90		
					(1.3724)[c]	89	2.5	9
Trimethylammonium[b]	7.3	.028	1.99	67	1.3716	98		
	7.3	.028	2.07	71	1.3713	100		
					(1.3715)[c]	98	1	1

[a] 1.0 *M* potassium ethoxide at 80°. [b] 4.0 *M* potassium ethoxide at 130–135°. [c] Analysis by infrared. The $n^{20}D$ value in parentheses is the calculated value based on the infrared analysis and is to be compared with the experimental value immediately above.

utilized, while *trans*-2-pentene was based on the peaks at 7.8 and 10.37 μ. We estimate the error in determining 1- and *trans*-2-pentene to be less than 3% and for *cis*-2-pentene to be 1.5%.

In general excellent agreement was realized between the refractive index and infrared procedures for the 1-olefin content of the products.

Elimination of 2-Pentyl Tosylate.—The solvolysis of 2-pentyl tosylate in anhydrous ethanol at its boiling point was found to have a half-life of 100 min., whereas the reaction with 1 *M* potassium ethoxide at the same temperature was complete in 5 min. Accordingly, it was considered that the solvolysis provided a negligible contribution to the reaction. In a typical elimination experiment 12.0 g. (0.494 mole) of 2-pentyl tosylate was added to a solution of 4.0 g. of potassium in 100 ml. of ethanol. The reaction mixture was heated under reflux in a Todd micro column and olefin removed as it appeared at the top of the column (2.7 ml. in 30 min.). The olefin was washed several times with ice-water and dried. The olefin (1.6 g., 50% yield) had $n^{20}D$ 1.3761, corresponding to 48% of 1-pentene. Infrared analysis showed 48% 1-, 18% *cis*-2- and 34% *trans*-2-pentene.

Elimination of 2-Pentyldimethylsulfonium Iodide.—The procedure for separation of dimethyl sulfide and pentenes was tested as follows. A mixture of 2.70 g. of dimethyl sulfide and 3.93 g. of 1-pentene was added to 200 ml. of saturated aqueous mercuric chloride at 0°. After standing for 0.5 hour, the pentene was slowly removed in vacuum into a −80° trap. The recovered 1-pentene weighed 3.53 g., a recovery of 90%. Its refractive index, $n^{20}D$ 1.3718, was essentially identical with that of the original material, $n^{20}D$ 1.3717. The mercuric chloride complex ($3HgCl_2 \cdot 2Me_2S$)[16] weighed 19.30 g., corresponding to a 95% recovery of the dimethyl sulfide.

A synthetic mixture of trimethylsulfonium iodide and 1-pentene was treated with potassium ethoxide. The dimethyl sulfide was removed as described above. The residual olefin and methyl ethyl ether fraction was washed repeatedly at 0° to remove the ether. After 30 washings the refractive index was constant at 1.3717, as compared to the original value of $n^{20}D$ 1.3718.

In the elimination experiment 10.0 g. of 2-pentyldimethylsulfonium iodide was treated with a solution of 4.0 g. of potassium in 100 ml. of ethanol. The distillate, 4.45 g. in 2 hr., was separated. It yielded 11.00 g. of dimethyl sulfide–mercuric chloride complex, equivalent to a 66% yield of the sulfide. After applying the washing procedure there was obtained 1.48 g. of pentene (60% yield), $n^{20}D$ 1.3728, corresponding to 85% 1-pentene.

Elimination of 2-Pentylmethyl Sulfone.—Negligible reaction was observed in 24 hours with 1 *M* potassium ethoxide. In di-*n*-amyl ether at 185° the reaction was essentially complete in 5 min. 4 *N* Potassium ethoxide at 130° gave a reasonable rate of reaction and this was adopted for the elimination study.

2-Pentylmethyl sulfone, 7.7 g., was added to a solution of 8 g. of potassium in 50 ml. of ethanol. The reaction mixture was heated at 130–135° for 32 hours. The olefin was washed with water and dried. There was obtained 1.40 g., representing a yield of 39%. The refractive index, $n^{20}D$ 1.3723, corresponds to a composition of 90% 1-pentene. Infrared analysis indicates the composition to be 89% 1-, 2.5% *cis*-2- and 9% *trans*-2-pentene.

Elimination of 2-Pentyltrimethylammonium Iodide.—In a typical experiment 7.3 g. of 2-pentyltrimethylammonium iodide was added to 100 ml. of 4 *M* potassium ethoxide. The material was heated at 130–135° for 5 hours and the distillate fractionated in a Todd micro column. The distillate was collected in a U-tube at 0° over water. The olefin layer was washed several additional times and the combined washings were titrated for trimethylamine. A 71% yield of the base was indicated. The product was again thoroughly washed with water at 0° to remove methyl ethyl ether. There was obtained 1.99 g. (67% yield) of pentene, $n^{20}D$ 1.3713, corresponding to a composition of 100% 1-pentene. Infrared analysis indicated 98% of 1-pentene with roughly 1% each of the *cis*- and *trans*-2-.

The experimental data are summarized in Table II.

Acknowledgment.—We are indebted to the Upjohn Co. of Kalamazoo, Michigan, for the financial support which made this study possible. We are also indebted to the National Bureau of Standards for the standard samples of 1-, *cis*-2- and *trans*-2-pentene used in the infrared analyses and to Mr. B. C. Subba Rao for his assistance in the preparation of several of the necessary intermediates.

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[16] W. F. Faragher, J. C. Morrell and S. Comay, THIS JOURNAL, **51**, 2774 (1929).