

TABLE VI
SUMMARY OF EXPERIMENTAL DATA ON THE YIELD AND COMPOSITION OF OLEFINS FORMED IN THE DEHYDROHALOGENATION OF *t*-ALKYL BROMIDES WITH PYRIDINE AND POTASSIUM ETHOXIDE

Tertiary bromide, RCH ₂ CB ₂ (CH ₃) ₂	G.	Moles	Base, ml.	Olefin	Yield,	Olefin	Composition	
				g.	%	<i>n</i> _D ²⁰	1-%	2-%
<i>t</i> -Amyl bromide	15.10	0.10	100, 1.0 <i>M</i> EtOK	6.30	90	1.3847	29	71
	15.10	.10	100, 1.0 <i>M</i> EtOK	5.79	83	1.3846	28	72
	15.10	.10	100, 1.0 <i>M</i> EtOK	5.18	74	1.3843	32	68
	12.05	.08	80, pyridine	4.95	90	1.3850	25	75
	15.10	.10	100, pyridine	6.38	91	1.3850	25	75
2-Methyl-2-bromopentane	8.25	.05	50, 1.0 <i>M</i> EtOK	2.56	61	1.3958	51	49 ^a
	12.00	.067	100, 1.0 <i>M</i> EtOK	4.68	84	1.3960	49	51
	16.50	.10	100, pyridine	7.50	88	1.3975	32	68
2,4-Dimethyl-2-bromopentane	8.95	.05	50, 1.0 <i>M</i> EtOK	3.04	63	1.4010	54	46 ^a
	17.90	.10	100, pyridine	8.50	87	1.4015	44	56
2,4,4-Trimethyl-2-bromopentane	19.30	.10	100, 4.0 <i>M</i> EtOK	7.56	68	1.4096	86	14 ^a
	19.30	.10	100, pyridine	9.43	84	1.4107	71	29
	19.30	.10	100, pyridine	10.45	93	1.4108	70	30

^a The reaction mixture was poured into water, the olefin layer separated and distilled.

ice-bath and the washings were carried out at 0° by using an ice-water jacketed separatory funnel.

The isolation procedure was modified in the potassium ethoxide elimination reactions that produced olefins boiling near ethanol. The reaction mixture was poured into ice-water and the olefin fraction separated, washed with water and distilled, using pyridine or one of its higher homologs as a chaser. The olefin was again washed, thoroughly dried and analyzed. This procedure resulted in decreased yields of olefin, but no change in the isomer composition was observed.

Analysis was based primarily on refractive index measurements checked occasionally by infrared determinations. The refractive index values used for the individual components have been recorded previously.^{4b}

It was established earlier that the refractive indices of mixtures of 1- and 2-amylens fit a linear interpolation formula.¹¹ We established that the same holds for other olefins formed in the elimination reactions.

(11) M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2065 (1948).

Typical results are summarized in Table IV.

The extent of the agreement realized in the infrared checks of the reaction products obtained in these studies is indicated by the data in Table V.

All elimination procedures were carefully checked with synthetic mixtures of pure olefins to ensure that neither isomerization nor fractionation of the olefins was a significant factor in the composition of the olefins isolated from the reaction mixtures.

The experimental results are summarized in Table VI.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Elimination Reactions. VII. The Effect of the Steric Requirements of Alkoxide Bases on the Direction of Bimolecular Elimination

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The effect of the steric requirements of the attacking base on the direction of elimination has been studied by examining the products formed in treating representative secondary and tertiary bromides with the potassium salts of ethanol, *t*-butyl alcohol, *t*-amyl alcohol and triethylcarbinol in the respective alcohols as solvents. In the case of *t*-amyl bromide the percentage of 1-olefin in the product increases from 30 to 72, to 78, and finally to 89 for the four bases, respectively. Similar increases in the yield of the 1-olefin with increasing steric requirements of the alkoxide base were observed for 2-bromobutane, 2-bromopentane, 2,3-dimethyl-2-bromobutane and 2,4,4-trimethyl-2-bromopentane. Bimolecular rate data for the reaction of potassium *t*-butoxide with various alkyl bromides indicate that the increase in yield of the 1-olefin is primarily the result of a decrease in the rate of removal of the hydrogen in the hindered 3-position. It is therefore possible to shift elimination from essentially Saytzeff-type to essentially Hofmann-type by increasing the steric requirements of the attacking base.

According to the interpretation proposed in the previous paper,³ it should be possible to exercise some measure of control over the direction of the bimolecular elimination reaction by modifying the

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

steric requirements of the attacking base. In order to examine this possibility, a study was undertaken of the olefin distribution afforded by alkoxide bases of increasing steric requirements: C₂H₅O⁻, (CH₃)₂CO⁻, C₂H₅(CH₃)₂CO⁻ and (C₂H₅)₃CO⁻.⁴ In the course of this study it also proved of interest to establish the rates of the bimolecular reaction of potassium *t*-butoxide with a number of secondary and tertiary alkyl bromides. With these data it becomes

(4) A preliminary communication of the results was published previously: H. C. Brown and I. Moritani, *ibid.*, **75**, 4112 (1953).

possible to estimate the rate of development of the double bond in each of the two possible positions and to define the factor which is responsible for the change in the nature of the product.⁵

Results

Approximately 1 *M* solutions of the potassium alkoxides were prepared by dissolving the metal in the respective alcohols. Sufficient alkyl bromide was added to make the reaction mixture approximately 1 *M* in this component and the reaction mixture was maintained for 6 hours at 70 ± 10°. The olefin was then distilled out of the reaction mixture through a Todd micro-column, thoroughly washed with water and dried by magnesium sulfate. In the case of the di-isobutylenes, where the boiling point prevented their separation in this way from *t*-butyl alcohol, the olefin was recovered by dilution with water, followed by separation and distillation.

Refractive indices were utilized for analysis of the tertiary olefins, occasionally checked by infrared determinations.⁶ The three component mixtures obtained from the secondary olefins were analyzed by infrared.

In the case of the secondary bromides the rates of solvolysis in ethanol at 70° are negligible compared with their rates of reaction with potassium ethoxide in the concentrations used in the present experiments. Consequently, there is no doubt that the olefins obtained arise as a result of the bimolecular elimination mechanism.

In the case of *t*-amyl bromide the rate of solvolysis in ethanol at 25° is not negligible relative to its reaction with 1.0 *M* sodium ethoxide.⁷ We considered undertaking a detailed kinetic analysis of the reaction, similar to that made by Dhar, Hughes and Ingold. However, the first-order rate constants increase with increasing concentration of potassium ethoxide while the second-order constants decrease. As a result the analysis is neither simple nor entirely satisfactory. Consequently we adopted another approach in an attempt to establish whether the solvolysis reactions make major contributions to these elimination reactions.

The solvolysis of *t*-amyl bromide in ethanol at 25° under neutral conditions leads to the formation of 36% olefin.⁷ Solvolysis of *t*-amyl bromide at 70° leads to the formation of 48% olefin. In both cases it is presumed that the carbonium ions not going to olefin react with the solvent to form *t*-amyl ethyl ether.

In typical elimination experiments using 1 *M* potassium ethoxide the olefin recovery averaged 85%. This compares with an olefin recovery of 93% from a synthetic reaction mixture. Consequently, it appears that no more than 8% of the *t*-amylcarbonium ions can be going to form *t*-amyl ethyl ether. Since the solvolysis results show that roughly 50% of the *t*-amylcarbonium ions must be going to the ether, the contribution of the solvolysis reaction to the

total product can be estimated to be no more than 10–20%.

Dhar, Hughes and Ingold⁷ obtained a value of 28% 2-methyl-1-butene in the olefin product at 25°, after correcting for the contribution from the solvolytic reaction. We obtain an average value of 30% at 70°. Corrected for 10–20% contribution from the solvolytic reaction (20% 1-olefin at 70°) would raise this value to 31–32.5%. Since our estimated uncertainty in the analysis is ± 3%, it appeared to be an unnecessary refinement to attempt to correct for the relatively minor contributions from the unimolecular elimination.

In the case of 2,3-dimethyl-2-bromobutane the elimination was carried out with both 1.0 and 4.0 *M* potassium ethoxide. Almost identical olefin compositions were obtained. Consequently it appears safe to conclude that here also the unimolecular reaction can make no more than a minor contribution to the total reaction.

It was previously demonstrated that the solvolytic reaction is much less important in *t*-butyl alcohol than it is in ethanol.⁸ It was assumed that the importance of the solvolysis reaction would be even less in the higher alcohols. To the extent that there may be minor contributions from the solvolysis reactions, the figures for the percentage of 1-olefin in the product may be somewhat low. However, it is our belief that any error arising from the neglect of the contribution by the solvolysis reaction represents an error that is no larger than the 3% estimated uncertainty in the olefin analyses.

The experimental results are summarized in Table I.

TABLE I
COMPOSITION OF OLEFINS FORMED IN THE DEHYDROHALOGENATION OF ALKYL BROMIDES BY POTASSIUM ALKOXIDES

Alkyl bromide	1-Olefin in product, %			
	C ₂ H ₅ O -	(CH ₃) ₂ - CO -	(C ₂ H ₅) ₂ - CO -	(C ₂ H ₅) ₂ - CO -
2-Bromobutane	19 ^{a,b}	53		
2-Bromopentane	29 ^c	66		
2,3-Dimethyl-2-bromobutane	21	73	81	92
<i>t</i> -Amyl bromide	30 ^d	72.5	77.5	88.5
2-Methyl-2-bromopentane	50 ^d			
2,4-Dimethyl-2-bromopentane	54 ^d			
2,4,4-Trimethyl-2-bromopentane	86 ^d	98		97

^a H. J. Lucas, R. T. Dillon and W. G. Young, *THIS JOURNAL*, **52**, 1949 (1930). ^b L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2058 (1948). ^c H. J. Lucas, T. P. Simpson and J. M. Carter, *THIS JOURNAL*, **47**, 1462 (1925). ^d H. C. Brown, I. Moritani and M. Nakagawa, *ibid.*, **78**, 2190 (1956).

Rate measurements were then made for the bimolecular reaction of a number of representative alkyl halides with potassium *t*-butoxide in *t*-butyl alcohol solution at 25°. Relatively concentrated solutions, 1.0 *M* in each component, were utilized in order to minimize the importance of any concurrent unimolecular reaction of the halide.⁸ The results are summarized in Table II.

(8) H. C. Brown and I. Moritani, *THIS JOURNAL*, **76**, 455 (1954).

(5) For an alternative view of the factors controlling the direction of elimination reactions, see 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).

(6) See Tables IV and V, ref. 3.

(7) M. L. Dhar, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2065 (1948).

TABLE II
SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF
POTASSIUM *t*-BUTOXIDE WITH ALKYL HALIDES IN *t*-BUTYL
ALCOHOL AT 25°

Alkyl halide	Rate constants k_2 (l. mole ⁻¹ sec. ⁻¹) × 10 ⁶
Isopropyl bromide	2.35
2-Bromobutane	1.40
2-Bromopentane	0.781
<i>t</i> -Butyl bromide	5.62
<i>t</i> -Amyl chloride ^a	0.0578
<i>t</i> -Amyl bromide ^a	3.36
<i>t</i> -Amyl iodide ^a	23.4
2,4,4-Trimethyl-2-bromopentane	2.97
α -Phenylethyl bromide	15.4

^a Reference 8.

Discussion

In the dehydrohalogenation of 2-bromobutane there is observed an increase in the yield of 1-butene from 19% with ethoxide to 53.4% with *t*-butoxide. Similarly, 2-bromopentane exhibits an increase in the yield of 1-pentene from 29% in elimination with ethoxide to 66% for the *t*-butoxide.

Similar results are obtained in the case of the tertiary halides (Table I). Thus 2,3-dimethyl-2-bromobutane exhibits an increase in the yield of the 1-olefin from 21% for the ethoxide, to 73% for the *t*-butoxide, to 81% for the *t*-amyl oxide and finally to 93% for the potassium salt of triethylcarbinol. These same four bases produce an increase in the yield of 2-methyl-1-butene from *t*-amyl bromide of 30 to 72.5, to 77.5, and finally, to 88.5%.

Thus, there is realized a regular increase in the ratio of 1-/2-olefin in these elimination reactions with increasing steric requirements of the attacking base.

It is unfortunate that it is not possible to modify the steric requirements of these alkoxides without simultaneously modifying other factors as well. Thus it is quite probable that the base strengths increase simultaneously with the steric requirements. Moreover, the reactions were carried out in the respective alcohols as reaction medium. Consequently, the dielectric constant of the medium is likewise being altered. It is necessary to examine the possibility that these factors may influence the direction of elimination.

The role of the dielectric constant on the rate of elimination reactions has been examined by Hughes, Ingold and their co-workers.⁹ They find only a small decrease in the rate of the second-order reaction of isopropyl bromide and base with increasing aqueous content of the reaction medium. The effect is quite small for relatively major changes in the solvent. Thus a change in the solvent from 100% ethanol to 60-40 ethanol-water mixtures results in a decrease in the rate constant from 1.46 to 0.47. In the present experiments the change in the nature of the reaction medium is much smaller (e.g., ethanol to *t*-butyl alcohol). Moreover, there does not appear to be any reason to expect that a change in the reaction medium would not have very

(9) K. A. Cooper, M. L. Dhar, E. D. Hughes, C. K. Ingold, B. J. MacNulty and L. I. Woolf, *J. Chem. Soc.*, 2043 (1948).

similar effects on the rate of attack at the two possible positions. It appears therefore that we can eliminate the possibility that the nature of the reaction medium plays any significant role in modifying the ratio of the two isomeric olefins in the product.¹⁰

The elimination reactions here discussed represent a competition by the reagent for two possible reactive positions in the molecule. In such reactions an increase in the activity of the attacking species would be expected to result in a loss in selectivity. A highly active reagent should yield an isomer distribution approaching that predicted on the basis of a statistical attack on the available hydrogen atoms. However, with increasing basic strength of the alkoxide bases ($C_2H_5O^- < (CH_3)_3CO^-$) there is observed not a decrease, but rather an increase in the selectivity of the reagent. It may be concluded therefore that the increase in base strength does not play any major role in altering the isomer distribution in the present reaction.¹¹

In elimination with potassium ethoxide there is obtained 79% of 2,3-dimethyl-2-butene as compared to 70% of 2-methyl-2-butene. The 1-olefins in these two cases are quite similar structurally and must be of similar stability. The higher yield of the 2-olefin in the case of 2,3-dimethyl-2-butene must be the result of greater hyperconjugative stabilization of the incipient olefin by the four adjacent methyl groups, as compared to the lesser stabilization afforded by the three methyl groups in 2-methyl-2-butene. The results are therefore in excellent agreement with the theoretical basis for the Saytzeff rule as proposed by Hughes and Ingold and their co-workers.⁵

The elimination reaction requires the attack by the base on a tertiary hydrogen atom in 2,3-dimethyl-2-bromobutane as compared to a secondary hydrogen atom in 2-methyl-2-bromobutane. The former reaction should therefore be more sensitive to the steric requirements of the attacking base. In accordance with this interpretation it is significant that the situation observed with ethoxide is reversed with bases of higher steric requirements. With these bases smaller yields of the 2-olefin are realized from 2,3-dimethyl-2-bromobutane than is the case with 2-methyl-2-bromobutane (Table I).

By utilizing the rate data and the available results on the isomer distribution it is possible to calculate the rates of attack at each of the two types of hydrogen atoms in a given molecule. The results are summarized in Table III.

The high rate of reaction of the primary hydrogens of α -phenylethyl bromide as compared to those of the simple aliphatic secondary halides is further evidence as to the importance of resonance stabilization of the incipient olefin on the rate of the

(10) This conclusion is supported by the results of a study of the effect of the steric requirements of a series of pyridine bases on the olefin distribution. In these experiments the liquid pyridine bases constitute the reaction media. The differences in the dielectric properties of the different pyridine bases must be quite minor. However, there was also observed a regular shift from 2- to 1-olefin with increasing steric requirements of the base; H. C. Brown and M. Nakagawa, *THIS JOURNAL*, **78**, 2197 (1956).

(11) The possible effect of changes in base strength on the elimination reactions has been discussed recently: D. J. Cram, F. D. Greene and C. H. Depuy, *THIS JOURNAL*, **78**, 790 (1956).

TABLE III
RATE CONSTANTS^a FOR THE REACTION OF ETHOXIDE AND
t-BUTOXIDE WITH ALKYL BROMIDES

Compound	Rate constant $\times 10^4$, k_2 (l. mole ⁻¹ sec. ⁻¹)			
	Ethoxide		<i>t</i> -Butoxide	
	Prim.	Sec.	Prim.	Sec.
Isopropyl bromide	0.395		0.392	
2-Bromobutane	.217	1.41	.247	0.329
2-Bromopentane	.267	0.88	.171	.133
<i>t</i> -Butyl bromide	3.33		.624	
<i>t</i> -Amyl bromide	2.83	21	.407	.462
2,4,4-Trimethyl-2-bromopentane			.485	.029
α -Phenylethyl bromide			5.13	

^a Calculated per primary and secondary hydrogen atom using data from ref. 5 and Tables I and II.

elimination reaction.⁵ The faster rate of reaction of ethoxide ion with the primary hydrogens of the tertiary bromides as compared with those of the secondary derivatives may also be interpreted in this way—in these cases hyperconjugation provides the stabilization factor.⁵

In the case of the reaction with *t*-butoxide, the tertiary bromides remain faster than the secondary, but the difference is far smaller than that observed with ethoxide. It is probable that the larger steric factor in the tertiary halides results in a decrease in their reactivity relative to that of the less hindered secondary derivatives.

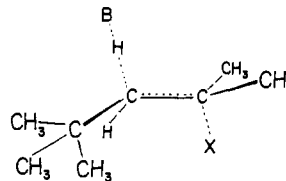
In their reaction with *t*-butoxide the primary hydrogen atoms also show a regular decrease in reactivity with increasing length of the chain: isopropyl > 2-butyl > 2-pentyl; *t*-butyl > *t*-amyl. This again may be attributed to increased steric strains in the transition state.

In the case of the secondary halides it appears

by the bulky base as compared to ethoxide ion.

In the tertiary halides there is observed a considerable decrease in the rate of attack of *t*-butoxide on the primary hydrogen atoms. However, there is an even greater decrease in the case of the secondary hydrogen atoms, accounting for the shift in isomer distribution.

The rate of attack of *t*-butoxide on the primary hydrogen of 2,4,4-trimethyl-2-bromopentane appears to be normal. The very low rate of attack of this base on the secondary hydrogen presumably arises from the difficulty in bringing the bulky *t*-butyl and X groups in close proximity while simultaneously bringing the bulky base within close proximity of the secondary hydrogen.



In conclusion, it appears that the available data are in agreement with the proposal that hyperconjugative stabilization of the incipient olefin results in eliminations in accordance with the Saytzeff rule.⁵ However, it also appears that steric effects in the transition state also constitute an important factor. Such strains can overcome the effects of hyperconjugative stabilization and achieve a transition from Saytzeff- to Hofmann-type elimination. Such strains may be introduced by increasing the steric requirements of the attacking base, providing a convenient means of controlling the direction of the elimination reaction.

TABLE IV
SUMMARY OF EXPERIMENTAL DATA ON THE YIELD AND COMPOSITION OF OLEFINS FORMED IN THE DEHYDROHALOGENATION
OF *t*-ALKYL BROMIDES WITH POTASSIUM ALKOXIDES

Alkyl bromide	G.		Base, ml.	Olefin, g.	Yield, %	Olefin composition n_D^{20}	
	G.	Moles				1, %	2, %
2-Bromobutane	13.70	0.100	150, 0.96 <i>M</i> <i>t</i> -BuOK			53	47
2-Bromopentane	15.10	.100	150, 0.96 <i>M</i> <i>t</i> -BuOK	6.33	90.6	1.3744	66 34
2,3-Dimethyl-2-bromobutane	8.33	.061	75, 1.0 <i>M</i> EtOK	3.55	82	1.4078	20 80
	16.50	.100	100, 1.0 <i>M</i> EtOK	7.31	87	1.4072	22.5 77.5
	16.50	.100	100, 4.0 <i>M</i> EtOK	8.05	93	1.4073	22 78
	16.50	.100	150, 1.0 <i>M</i> <i>t</i> -BuOK	7.74	90	1.3963	73 27
	16.50	.100	150, 1.0 <i>M</i> <i>t</i> -AmOK	7.92	94	1.3944	81 19
	16.50	.100	150, 1.0 <i>M</i> Et ₃ COK	6.91	82	1.3921	92 8
<i>t</i> -Amyl bromide	13.4	.089	60, ethanol ^a	3.0	48	1.3855	20 80
	15.1	.100	100, 1.0 <i>M</i> EtOK ^b	6.0	85 ^c	1.3844	31 69
	15.10	.100	100, 1.0 <i>M</i> <i>t</i> -BuOK	6.72	96	1.3805	72.5 27.5
	16.60	.114	150, 1.0 <i>M</i> <i>t</i> -BuOK	7.42	93	1.3805	72.5 27.5
	15.10	.100	210, 0.71 <i>M</i> <i>t</i> -AmOK	6.66	95	1.3800	77.5 22.5
	11.2	.074	90, 1.2 <i>M</i> Et ₃ COK	5.12	98	1.3789	88.5 11.5
2,4,4-Trimethyl-2-bromopentane	19.30	.100	100, 1.0 <i>M</i> <i>t</i> -BuOK	7.50	66.8	1.4087	99 1
	19.30	.100	150, 1.0 <i>M</i> <i>t</i> -BuOK	8.85	80	1.4088	97 3
	9.0	.047	50, 1.0 <i>M</i> Et ₃ COK	5.2	90	1.4088	97 3

^a Reaction mixture maintained neutral by slow addition of 1.2 *M* potassium ethoxide as solvolysis proceeded. ^b See Table VI, ref. 3, for additional experiments. ^c Under identical conditions recovery of olefin from synthetic reaction mixture was 93%.

that the rate of attack of the *t*-butoxide ion on primary hydrogen is similar to that of ethoxide ion. The marked shift in isomer distribution with *t*-butoxide as base arises primarily from a greatly reduced rate of attack on the secondary hydrogen atoms

Experimental Part

Materials.—The tertiary bromides were synthesized as previously described.¹² α -Phenylethyl bromide was pre-

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

pared by treating the alcohol with dry hydrogen bromide at 0° (b.p. 76.0° at 7 mm., n_D^{20} 1.5615). 2-Bromopentane was prepared by the method described by Pines¹³ (b.p. 117.5° at 734 mm., n_D^{20} 1.4401). Both isopropyl bromide (b.p. 58.0–59.0°, n_D^{20} 1.4248) and 2-bromobutane (b.p. 91°, n_D^{20} 1.4363) were commercial products which were carefully fractionated before use.

t-Butyl and *t*-amyl alcohol were commercial products also carefully fractionated before use. Triethylcarbinol was prepared by the action of ethylmagnesium bromide on diethyl carbonate (b.p. 74° at 61 mm., n_D^{20} 1.4261).

Elimination Experiments.—The following two experiments will illustrate the procedures used. A. 2,3-Dimethyl-2-bromobutane, 16.5 g. (0.100 mole), was added to 100 ml. of 1 *M* potassium ethoxide in absolute ethanol contained in a round-bottomed flask. The reaction mixture was attached to a Todd column and maintained at 70 ± 10° for 6 hours, removing olefin as it was formed. At the end of the reaction the temperature was raised and residual olefin (with minor amounts of ethanol) was removed. The distillate was washed with 15 ml. of ice-water in several portions and dried by magnesium sulfate. A total of 7.31 g. of olefin, representing a yield of 87%, was obtained. The refractive index, n_D^{20} 1.4072, indicated an analysis of 22.5% 1- and 77.5% 2-. The use of 4 *M* potassium ethoxide gave essentially identical results.

B. The 1 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol was prepared by adding 6 g. of metallic potassium

to 150 ml. of carefully purified *t*-butyl alcohol under a nitrogen atmosphere. The solution was heated to 75° and 19.3 g. (0.100 mole) of 2-bromo-2,4,4-trimethylpentane was added. The solution was heated for two hours at 75°. The solution was then poured into 500 ml. of cold water. The olefin layer was separated, washed several times with cold water and dried with magnesium sulfate. Five ml. of 2,6-lutidine was added to the olefin (to prevent isomerization by residual traces of the tertiary bromide remaining in the product and to serve as a chaser in the column) and the olefin was carefully distilled through the Todd column (b.p. 99–100.8° at 74.5 mm.). The product was again washed thoroughly with water and dried. There was obtained 8.85 g. of olefin, a yield of 80%. The refractive index, n_D^{20} 1.4088, indicated an isomer distribution of 97% 1- and 3% 2-.

The experimental results are summarized in Table IV.

Kinetic Studies of the Reaction of Potassium *t*-Butoxide with Alkyl Bromides.—The experimental procedures have been reported previously.⁶ The reactions were followed by the decrease in concentration of base. We were unable to detect any significant quantity of a displacement reaction. Consequently the observed second-order rate constant has been treated as the second-order constant for the elimination reaction. To the extent that there may exist as much as several per cent. of a displacement reaction in some of the cases, the rate constants for the elimination reaction may be slightly high. The rate constants are summarized in Table II.

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(13) H. Pines, A. Rudin and V. N. Ipatieff, *THIS JOURNAL*, **74**, 4063 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Elimination Reactions. VIII. The Effect of the Steric Requirements of Pyridine Bases on the Direction of the Elimination Reaction

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The effect of the steric requirements of the attacking base on the direction of elimination has been studied by examining the products formed in treating representative tertiary bromides with pyridine, 2-picoline and 2,6-lutidine. Treatment of *t*-amyl bromide with pyridine produces 25% of the 1-olefin. Essentially identical results are obtained with 4-picoline. However, the yield of 1-olefin rises to 30% with 2-picoline and to 45% with 2,6-lutidine. Similar increases in the ratio of 1-/2-olefin with increasing steric requirements of the pyridine base have been observed for 2,3-dimethyl-2-bromobutane, 2-methyl-2-bromopentane, 2,4-dimethyl-2-bromopentane and 2,4,4-trimethyl-2-bromopentane. Shifts from Saytzeff-type toward Hofmann-type elimination can be achieved by an increase of the steric requirements of the base, either alkoxide or pyridine in nature.

In the previous paper it was demonstrated that an increase in the steric requirements of the alkoxide base results in an increase in the ratio of 1-/2-olefin in the product obtained by the dehydrobromination of 2-bromoalkanes.² It was pointed out that the increase in steric requirements of the alkoxide base was accompanied both by a change in the nature of the reaction medium and by a change in the strength of the base.

Arguments were presented that neither of these factors could be playing a very important role in the results. However, it appeared desirable to obtain confirmatory data. Consideration of the problem suggested that a study of the effect of pyridine bases of varying steric requirements would provide a test of the generality of the proposed interpretation while avoiding the difficulties inherent in the use of the alkoxides. Accordingly, a study was undertaken of the effect of the increasing steric re-

quirements of a series of heterocyclic bases, pyridine, 2-picoline, 2,6-lutidine, on the direction of the elimination reactions in a series of tertiary bromides. In order to examine the possible role of base strength on the reaction, several experiments were carried out using 4-picoline as the base.

Results

The experiments were carried out by introducing the tertiary bromide, usually 0.100 mole, into the base, usually 100 ml. Experiments showed that the olefin distribution was not sensitive to the reaction temperature (70–130°) within the limits of accuracy of the analytical procedure. For example in elimination of *t*-amyl bromide by 4-picoline at several temperatures the product contained 23% of the 1-olefin at 70°, 25% at 100°, and 25% at 130°. Accordingly, the procedure was adopted of taking the reaction mixture rapidly up to the reflux temperature and removing the olefin in a micro fractionating column as rapidly as it was formed. The olefin was washed with water and analyzed by measurement of its refractive index.

(1) Post-doctorate Assistant at Purdue University, 1953–1954, on a contract supported by the Office of Naval Research and a grant provided by the National Science Foundation.

(2) H. C. Brown, I. Moritani and Y. Okamoto, *THIS JOURNAL*, **78**, 2193 (1956).