pared by treating the alcohol with dry hydrogen bromide at 0° (b.p. 76.0° at 7 mm., n^{20}_D 1.5615). 2-Bromopentane was prepared by the method described by Pines[13] (b.p. 117.5° at 734 mm., n^{20}_D 1.4401). Both isopropyl bromide (b.p. 58.0–59.0°, n^{20}_D 1.4248) and 2-bromobutane (b.p. 91°, n^{20}_D 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^{20}_D 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^{20}_D 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^{20}_D 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.

LAFAYETTE, INDIANA

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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

BY HERBERT C. BROWN AND M. NAKAGAWA[1]

RECEIVED OCTOBER 26, 1955

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 wih 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 requirements 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.

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[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).

The results are summarized in Table I.

TABLE I

COMPOSITION OF OLEFINS FORMED IN THE DEHYDROHALOGENATION OF ALKYL BROMIDES BY PYRIDINE BASES

Alkyl bromide	1-Olefin in product, %			
	4-Picoline	Pyridine	2-Picoline	2,6-Lutidine
2,3-Dimethyl-2-bromobutane		10	18	37.5
t-Amyl bromide	25[a] 23[b] 25[c] 25[d]	25[e]	30	44.5
2-Methyl-2-bromopentane		32[e]	39	48
2,4-Dimethyl-2-bromopentane		44[e]	52	58
2,4,4-Trimethyl-2-bromopentane		70[e]	74	81

[a] Usual procedure of distilling olefin as it was formed at the reflux temperature. [b] 70°. [c] 100°. [d] 130°. [e] H. C. Brown, I. Moritani and M. Nakagawa, THIS JOURNAL, **78**, 2190 (1956).

TABLE II

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

Tertiary bromide, RCBrC(CH$_3$)$_2$			Base, ml.	Olefin, g.	Yield, %	Olefin composition		
	G.	Mole				$n^{20}D$	1-, %	2-, %
2,3-Dimethyl-2-bromobutane	16.50	0.10	100, pyridine	7.17	83	1.4100	10	90
	16.50	.10	100, pyridine	7.16	82	1.4100	10	90
	16 50	.10	100, 2-picoline	8.07	93	1.4087	18	82
	16.27	.097	100, 2,6-lutidine	7.41	91	1.4040	37	63
	16.50	.10	100, 2,6-lutidine	7.18	84	1.4039	38	62
t-Amyl bromide	15.10	.10	100, 4-picoline	6.46	93	1.3850	25	75
	15.10	.10	100, 4-picoline	6.35	91	1.3852	23	77[a]
	15.10	.10	100, 4-picoline	6.38	91	1.3850	25	75[b]
	15.10	.10	100, 4-picoline	6.35	91	1.3850	25	75[c]
	15.10	.10	100, 2-picoline	6.66	95	1.3845	30	70
	15 10	.10	100, 2,6-lutidine	6.03	86	1.3831	45	55
	15.10	.10	100, 2,6-lutidine	6.43	92	1.3832	44	56
2-Methyl-2-bromopentane	8.25	.050	50, 2-picoline	3.88	93	1.3969	39	61
	16.50	.10	100, 2,6-lutidine	8.13	96	1.3961	48	52
2,4-Dimethyl-2-bromopentane	8.95	.050	50, 2-picoline	4.60	94	1.4011	52	48
	10.02	.056	100, 2,6-lutidine	5.11	93	1.4008	58	42
2,4,4-Trimethyl-2-bromopentane	19.30	.10	100, 2-picoline	9.63	86	1.4105	74	26
	19.30	.10	100, 2,6-lutidine	10.02	90	1.4100	81	19
	5.00	.026	35, 2,6-lutidine	2.40	82	1.4100	81	19
	5 00	.026	50, 2,6-lutidine	2.47	85	1.4099	82	18

[a] 70° for 3 hours. [b] 100° for 1.5 hours. [c] The bromide was added slowly to the base at 130°.

Discussion

4-Picoline (pK_a 6.02) is a considerably stronger base than pyridine (pK_a 5.17).[3] Yet the isomer distributions realized in the dehydrohalogenation of *t*-amyl bromide are identical (Table I).

On the other hand, the use of 2-picoline (pK_a 5.97) results in a small but consistent increase in the ratio of 1-/2-olefin in the various products. Moreover, the more hindered base, 2,6-lutidine, (pK_a 6.75) brings about a more marked increase in the 1-olefin content of the dehydrohalogenation product.

In view of the identical results realized with pyridine and 4-picoline it appears reasonable to exclude the possibility that these changes in the amount of 1-olefin in the product are due to changes in the strengths of the different pyridine bases. Moreover, the dielectric constants of 4-picoline, 2-picoline and 2,6-lutidine must be so similar that it also appears reasonable to exclude this factor from consideration.

On the other hand, it is well established that the steric requirements of 2-picoline are considerably greater than those of pyridine, with those of 2,6-lutidine greater still.[4,5] Moreover, the steric effects of the second methyl group in 2,6-lutidine are considerably greater than the first. This corresponds to the observation that the second methyl group (in 2,6-lutidine) in general results in a considerably larger increase in the content of 1-olefin in the products than the first such group (in 2-picoline).

One further criterion can be applied. In the previous paper it was pointed out that the removal of a tertiary hydrogen in the elimination reaction, such as in the dehydrohalogenation of 2,3-dimethyl-2-bromobutane, should be more sensitive to the steric requirements of the base than the removal of a secondary hydrogen, as in the dehydrohalogenation of *t*-amyl bromide. This is evident in the present results. The increase in the 1-olefin with increasing steric requirements of the base is significantly steeper for 2,3-dimethyl-2-bromobutane than it is in *t*-amyl bromide.[6]

Consequently, it appears reasonable to conclude that the increase in the 1-olefin observed in the series of bases, pyridine, 2-picoline and 2,6-lutidine, must be due to the increasing steric requirements of these bases.

The changes in the 1-olefin content achieved in this series are somewhat less than those realized with the alkoxide bases. In part this must be due

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(3) H. C. Brown and F. X. Mihm, THIS JOURNAL, **77**, 1723 (1955).

(4) H. C. Brown, H. I. Schlesinger and S. Z. Cardon, *ibid.*, **64**, 325 (1942); H. C. Brown and G. K. Barbaras, *ibid.*, **69**, 1137 (1947).

(5) R. G. Pearson and F. V. Williams, *ibid.*, **75**, 3073 (1953).

(6) Quantitative expression of this trend may be had by comparing the ratios: 2,3-dimethyl-2-bromobutane: (1-/2- for 2,6-lutidine/1-/2- for pyridine) = 5.4; *t*-amyl bromide: (1-2- for 2,6-lutidine/1-/2- for pyridine) = 2.4.

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

BY HERBERT C. BROWN AND OWEN H. WHEELER[1]

RECEIVED OCTOBER 26, 1955

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.