[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Reaction of Certain Amines with Ethyl β-Bromopropionate and *n*-Butyl Bromide[1]

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In a previous paper[2] it was suggested that the mechanism of the elimination of hydrogen bromide from ethyl β-bromopropionate by piperidine is, first, the removal of a proton from the α-carbon atom of the ester, followed by the release of a bromide ion from the molecule. On the basis of such a mechanism it seemed that the effectiveness of a reagent in bringing about this elimination reaction would be a function of its basicity, and in this connection it was noted that Segaller[3] found that the reagents which he studied stood in the order, potassium hydroxide < sodium ethoxide < sodium phenoxide < sodium nitrophenoxide, in their ability to form isobutylene from tertiary butyl iodide. The suggestion also was made that the rate-determining factor in the reaction between piperidine and a bromide, which results in the replacement of a halogen by the piperidino radical to form a tertiary amine, is the ability of the piperidine to approach the carbon carrying the halogen. On the basis of such a mechanism, the replacement reaction would not be as dependent upon the basicity of the amine as would the elimination reaction. It seemed that these suggestions might be tested by a study of the reactions of other organic bases of different basicities with ethyl β-bromopropionate and *n*-butyl bromide. It has been shown that the elimination of hydrogen bromide does not occur with the latter compound to any appreciable extent with such reagents as piperidine[4] and pyridine.[5]

This paper reports the results obtained from a study of the reaction of five secondary amines and six tertiary amines with both ethyl β-bromopropionate and *n*-butyl bromide.

General Procedure.—The extent and course of the reaction for each secondary amine with ethyl β-bromopropionate and *n*-butyl bromide was determined by the procedure described in a previous paper[4] with the exception that carbon bisulfide[6] was used to determine the unreacted secondary amine in the case of piperidine, 2-methylpiperidine and diethylamine. It was found necessary to use phenyl isocyanate[4] with N-methylbenzylamine and methylaniline in order that a crystalline precipitate suitable for weighing be obtained. A second exception to the procedure was found necessary with methylaniline. The secondary amine hydrobromide formed as an oil which solidified when cooled in ice. This solid was dissolved in water and shaken with petroleum ether to remove any occluded methylaniline. This petroleum ether extract, after drying over anhydrous sodium sulfate, was added to the original reaction solution for the removal of any unreacted secondary amine. The water solution of the hydrobromide was made up to a volume of 100 cc. An aliquot was titrated with standard sodium hydroxide solution and a similar aliquot by the Volhard method for bromide. The two results checked within the limits of experimental error, indicating no appreciable quaternary salt formation.

A ratio of 0.02 mole of amine to 0.01 mole of the bromide was used in each case. The reactions were run at 90°.

The extent and course of the reaction of the various secondary amines with ethyl β-bromopropionate and *n*-butyl bromide are summarized in Table I. The values in columns A and B were determined from the amount of secondary amine hydrobromide which precipitated in the reaction tube. Values in column C represent the amount of unreacted amine as determined by precipitation with carbon bisulfide or phenyl isocyanate. Column D shows the calculated amount of tertiary amine formed assuming that the secondary amine originally put into the reaction, and not represented in columns B and C, had reacted to form a tertiary amine. In Table II the extent and course of the reaction of the tertiary amines with the two bromo compounds are summarized. The relative amount of tertiary amine salt and quaternary salt formed in each case was determined by titration of one aliquot of an aqueous solution of the precipitated salt with standard silver nitrate solution and another aliquot with standard alkali according to the method of Noller and Dinsmore.[5]

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[1] This work was supported in part by a grant from the Wisconsin Alumni Research Foundation.

[2] Drake and McElvain, THIS JOURNAL, **56**, 697 (1934).

[3] Segaller, *J. Chem. Soc.*, **103**, 1421 (1913).

[4] Semb and McElvain, THIS JOURNAL, **53**, 690 (1931).

[5] Noller and Dinsmore, *ibid.*, **54**, 1032 (1932).

[6] Drake and McElvain, *ibid.*, **55**, 1155 (1933).

The basicities of the amines used are listed in Tables I and II as pK_H and, with the exception of N-methylpiperidine, these values are those reported by Hall and Sprinkle.[7] The basicity of the latter amine was estimated colorimetrically (see footnote, Table II).

TABLE I

EXTENT AND COURSE OF REACTION AT 90° BETWEEN VARIOUS SECONDARY AMINES AND ETHYL β-BROMOPROPIONATE

Amine	pK_H	Reaction time, hrs.	A % reaction	B moles × 10^2 amine hydrobromide	C moles × 10^2 unreacted amine	D moles × 10^2 tert. amine 2 − (B + C)
Piperidine	11.13	0.25	98	0.98	0.18	0.84
2-Methylpiperidine	10.98	.25	95	.95	.72	.33
Methylaniline	4.85	5.5	36	.36	1.25	.39
Methylbenzylamine	9.58	0.25	85	.85	0.73	.42
Diethylamine	10.98	.25	92	.92	.44	.64
		n-Butyl Bromide				
Piperidine	11.13	48	88	0.88	0.21	0.91
2-Methylpiperidine	10.98	48	47	.47	1.06	.47
Methylaniline	4.85	48	58	.58	0.83	.59
Methylbenzylamine	9.58	48	73	.73	.53	.74
Diethylamine	10.98	48	42	.42	1.13	.45

TABLE II

EXTENT AND COURSE OF REACTION AT 90° BETWEEN VARIOUS TERTIARY AMINES AND ETHYL β-BROMOPROPIONATE

Amine	pK_H	Reaction time, hr.	Total reaction, %	Tertiary amine salt, %	Quaternary salt, %
Pyridine	5.19	5.5	33	8	25
N-Methylpiperidine	10.50[a]	0.25	58	58	0
N-Ethylpiperidine	10.41	.25	25	25	0
N-Ethylpiperidine		5.5	93	93	0
N-Butylpiperidine	10.48	0.25	19	19	0
N-Butylpiperidine		5.5	90	90	0
Dimethylaniline	5.16	336	89	30	59
Diethylaniline	6.56	336	24	24	0
		n-Butyl Bromide			
Pyridine	5.19	48	46	0	46
N-Methylpiperidine	10.50[a]	48	19	0	19
N-Ethylpiperidine	10.41	48	4	0	4

[a] Determined colorimetrically using alizarin yellow as an indicator. A comparison was made between equal concentrations of a solution of N-methylpiperidine and solutions of *n*-butylpiperidine and piperidine at one-third, one-half and two-thirds neutralization with standard hydrochloric acid. From this comparison the pK_H of N-methylpiperidine was estimated as approximately 10.50.

Discussion of Results

Consideration of the results summarized in Table I leads to the conclusion that the basicity of the amine is the controlling factor in the reaction involving the elimination of hydrogen bromide. With ethyl β-bromopropionate the stronger bases give a high per cent. of reaction in fifteen minutes while the weak base, methylaniline, reacts only to the extent of 36% in 5.5 hours. It is also interesting to note that while the stronger secondary bases remove hydrogen bromide with about equal facility from the bromo ester molecule, there is a considerable difference in the rates of their addition to the resulting acrylic ester, as shown by the amount of tertiary amine formed in each case (column D). This difference in rate of addition is undoubtedly due to steric factors associated with the structure of the amine.

The extent to which each of these secondary amines reacts with *n*-butyl bromide to produce a tertiary amine is apparently unrelated to its basicity. For example, methylaniline reacts to greater extent in forty-eight hours than does either of the much stronger bases, 2-methylpiperidine and diethylamine, while two bases, piperidine and diethylamine, of approximately equal strength show widely different reactivities.

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[7] Hall and Sprinkle, THIS JOURNAL, **54**, 3469 (1932).

This variation in reactivity of the different secondary amines with *n*-butyl bromide is probably due, as is their variation in rate of addition to acrylic ester, to steric factors associated with their structure and is in harmony with the suggestion that the rate-controlling factor in the replacement reaction is the ability of the amine to approach the carbon atom carrying the halogen.

In general, similar conclusions may be drawn from the results, listed in Table II, obtained with tertiary amines. In the reactions with ethyl β-propionate the extent of the reaction is definitely related to the basicity of the amine (*cf.* amount of tertiary amine salt produced with pyridine and the N-substituted piperidines after the 5.5 hours reaction period). However, within a group of related amines of approximately the same basicity there appears to be some steric factor involved in this elimination reaction, for piperidine (Table I) and the N-substituted piperidines (Table II) show widely different percentages of reaction with the bromo ester after a fifteen-minute reaction period. In this group the reactivity decreases as the size of the group attached to the piperidine nitrogen atom increases.

It was surprising to find that both pyridine and dimethylaniline give considerable amounts of the quaternary salt with the bromo ester. This reaction is not related to the elimination reaction[5] and its occurrence in these cases greatly complicates the interpretation of the results.

The extent of formation of the quaternary salts between butyl bromide and each of the three tertiary amines studied (Table II) is obviously independent of the basicity of the amine. These results parallel those obtained from the reaction of the secondary amines with butyl bromide (Table I) and it is not unlikely that the variations are due to the same causes.

Summary

A study of the rate and course of reaction of ethyl β-bromopropionate and *n*-butyl bromide with a number of secondary and tertiary amines of different basicities has been made. The results obtained lend support to previously suggested mechanisms for the elimination of hydrogen bromide and for the replacement of a bromine atom in an organic molecule by a secondary amino residue.

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Rearrangement During Pyrolysis of the Butenes

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1-Butene and 2-butene are the simplest olefins to possess the possibility of rearrangement. Therefore, the study of their pyrolysis is particularly significant. It was anticipated that other products would accompany the rearrangement products for the generalization has been established that olefins pyrolyze bidirectionally into simpler compounds and into more complex ones. With isomerization included, this would establish a tridirectional mechanism. Wheeler and Wood,[1] in the only prior work on 1- and 2-butene, have shown 2-butene to be somewhat the more stable isomer at 600°, but no difference in stability was noticed at 650–900° where extensive decomposition took place. Their attention was directed especially to the reaction liquids, which were chiefly cycloalkenes and cycloalkadienes. They gave no consideration to the study of rearrangement. Because of their work on the liquids we omitted them in our study.

To study the problem of rearrangement it was necessary to start with butenes of very high purity and it was even more essential to possess an analytical procedure capable of detecting the several C_4-hydrocarbons in the presence of each other. The absorption method[2] fails because 1-butene, 2-butene, butadiene and propylene all dissolve in the same reagent (83% sulfuric acid). The usual type of Podbielniak fractional distillation serves to separate the C_1, C_2, C_3 and C_4 hydrocarbons into these four groups but it lacks the precision necessary to separate the C_4 compounds individually. The boiling points of these gases are (°C.): 1-butene -6.7, methylpropene (isobutylene) -6.6, butadiene -2.6, butane 0.0, *cis*-2-butene $+0.3$, *trans*-2-butene[3] $+3.0$.

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[1] Wheeler and Wood, *J. Chem. Soc.*, 1819 (1930).

[2] Hurd and Spence, THIS JOURNAL, **51**, 3357 (1929).

[3] Schmitt and Boord, *ibid.*, **54**, 756 (1932), show that among olefin isomers with similar skeletons the one with the double bond most deeply buried in the molecule has the highest boiling point. They suggest, therefore, that the *trans*-2-butene should be higher boiling than the *cis*-.