2′-(3-Piperidino-1-hydroxypropyl)-fluorene.—Reduction of the ketones was carried out in the Parr apparatus using 5 g. of substance in 250 cc. of alcohol, 0.1 g. of platinum oxide catalyst and hydrogen under an initial pressure of 55 lb. per sq. in. The reaction was slow, generally requiring twenty-four hours. After filtration the solution was evaporated to one-half its volume or dry ether was added to the warm solution until cloudiness developed. The yield of the substance mentioned above was 62% and the pure compound melted at 217°. The reduced compounds were considerably more soluble than the ketones but had less physiological activity.

Potassium 2′-(3-Piperidino-1-oxopropyl)-fluorene-7′-sulfonate was prepared by adding 10 g. of 2′-(3-piperidino-1′-oxopropyl)-fluorene hydrochloride to 100 g. of concentrated sulfuric acid. The mixture was stirred at room temperature for two hours during which time solution occurred and a green-brown color resulted. On pouring onto ice, the sulfonic acid precipitated in an unfilterable colloidal state. It was warmed to 80° and diluted to 1.5 liter. Potassium hydroxide (25% solution) was added until a clear solution resulted. The addition of potassium chloride caused the potassium salt to separate. It was recrystallized from hot water. An aqueous solution of the potassium salt first gave a precipitate with hydrochloric acid and then dissolved in an excess of acid.

ω-Bromo-2-acetylfluorene.—A suspension of 20.8 g. of 2-acetylfluorene in 1000 cc. of anhydrous ether was cooled to 0° and 5 cc. of bromine in 200 cc. of anhydrous ether was added. The mixture was stirred for two hours at 0° and then allowed to warm up to room temperature. The bromine color had completely disappeared. The gray precipitate was filtered off and a further quantity was obtained by the evaporation of the mother liquor. These were combined and recrystallized from alcohol, yield 17.8 g. (62%). It was slightly soluble in ether, moderately soluble in alcohol and insoluble in water.

ω-Bromo-2-acetylfluorenone was prepared similarly with a yield of 63.1%. It was somewhat less soluble. On oxidation fluorenone-2-carboxylic acid melting at 335–340°[4] and giving no test for halogen was obtained. Substitution must have occurred in the side chain.

ω-Piperidino-2-acetylfluorene Hydrochloride.—This compound was obtained by reacting omega-bromo-2-acetylfluorene with piperidine in absolute ether and treating the solution with an excess of ethereal hydrogen chloride. A yield of 47.4% was obtained. It was slightly soluble in water and fairly soluble in alcohol.

Summary

Side chain amines of fluorene of the following types have been prepared; $2\text{-}C_{13}H_9COCH_2CH_2NR_2{\cdot}HCl$, $2\text{-}C_{13}H_9CHOHCH_2CH_2NR_2{\cdot}HCl$ and $2\text{-}C_{13}H_9COCH_2NR_2{\cdot}HCl$. When R_2 was morpholino or piperidino the yields in the Mannich reaction were excellent. The solubility of most of the compounds in water was low. Sulfonation increased the solubility but destroyed the anesthetic property.

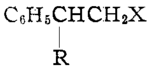
CINCINNATI 21, OHIO RECEIVED NOVEMBER 16, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

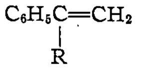
The Removal of Hydrogen Bromide from Certain β-Phenylalkyl Bromides by Means of Potassium Amide in Liquid Ammonia[1,2]

BY CHARLES R. HAUSER, PHILIP S. SKELL,[2a] ROBERT D. BRIGHT AND W. B. RENFROW

Alcohols or bromides of type (I) exhibit a considerable tendency to undergo rearrangement of the carbon skeleton, especially in the presence of acidic reagents. Thus, on dehydration in the presence of phosphorus pentoxide or infusorial earth, alcohols of this type produce mainly rearranged olefins (III).[3] Amagat[4] has reported that, even in the presence of sodium amide in boiling xylene, bromides of type (I) produce largely rearranged olefins; however, the conclusion that the base effects the rearrangement is not warranted.


$C_6H_5\underset{\textstyle R}{\underset{|}{C}}HCH_2X$

(I)


$C_6H_5\underset{\textstyle R}{\underset{|}{C}}{=}CH_2$

(II)

$C_6H_5CH{=}CHR$

(III)

Although acidic reagents might be expected to bring about rearrangement, strong bases such as the amide ion should not.[5] An acidic reagent attacks and removes the X with its bond pair of electrons allowing rearrangement to occur,[6] whereas the amide ion would generally be expected to attack the β-hydrogen effecting β-elimination[7,8] without rearrangement.[9] In the present investigation it has been found that, with potassium amide in liquid ammonia, bromides of type (I) in which R is methyl or ethyl eliminate hydrogen bromide practically without rearrangement of the carbon skeleton to form olefins of type (II). Some substitution product ($I, X = NH_2$) is also formed but its yield is very low (< 1%).

The bromide in which R is methyl, 2-phenyl-1-bromopropane (IV), was synthesized as represented by the series of reactions

$$C_6H_5CH_2CN \xrightarrow[\text{or } (C_6H_5)_3CNa \text{ in ether}]{\text{Na or } NaNH_2 \text{ in liq. } NH_3}$$

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[1] This work was supported in part by a grant from the Duke University Research Council.

[2] Reported at the Boston meeting of the American Chemical Society, September, 1939.

[2a] Present address: University of Chicago, Chicago, Illinois.

[3] Ramart and Amagat, *Ann. chim.*, **8**, 263 (1927).

[4] Amagat, *Bull. soc. chim.*, **49**, 1410 (1931).

[5] Sabetay (*Bull. soc. chim.*, **47**, 614 (1930)) has reported that an alcohol of type (I), 2-phenylpropanol-1, on slow distillation over anhydrous potassium hydroxide forms the unrearranged olefin, α-methylstyrene, but no yield was given.

[6] See especially Whitmore, THIS JOURNAL, **54**, 3274 (1932).

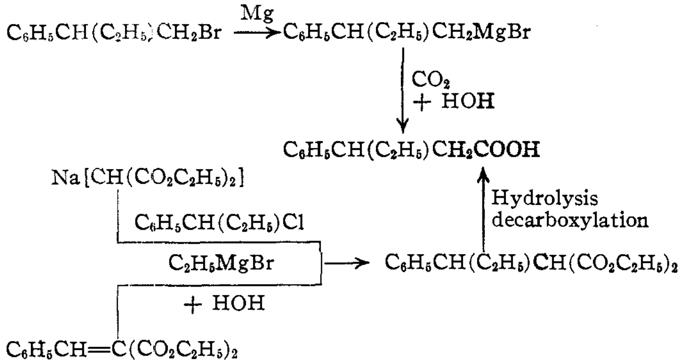
[7] See Hughes and Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

[8] After the completion of the present work (see ref. 2) evidence was obtained in this Laboratory (from a study of the elimination reaction using alkyl halides containing deuterium) that, even with alkyl halides containing β-hydrogen, the amide ion is capable of removing α-hydrogen effecting α-elimination which may be accompanied by rearrangement (see ref. 9). However, since only a little rearrangement of the carbon skeleton was observed in the present investigation, α-elimination either did not occur to an appreciable extent or was accompanied by the shift of the β-hydrogen to the α-carbon.

[9] See Hauser, THIS JOURNAL, **62**, 933 (1940).

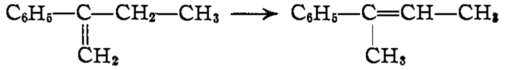
$$\begin{aligned}&[C_6H_5CHCN]Na \xrightarrow{CH_3I} C_6H_5CH(CH_3)CN \xrightarrow{HOH}\\ &C_6H_5CH(CH_3)COOH \xrightarrow[+NH_3]{SOCl_2}\\ &C_6H_5CH(CH_3)CONH_2 \xrightarrow{(H)}\\ &C_6H_5CH(CH_3)CH_2OH \xrightarrow{PBr_3}\\ &\qquad C_6H_5CH(CH_3)CH_2Br \quad (IV)\end{aligned}$$

The bromide in which R is ethyl, 2-phenyl-1-bromobutane (V), was synthesized in a similar manner starting with the carboxylic acid, which was commercially available. When freshly prepared, both of the bromides gave no immediate precipitate with aqueous silver nitrate; this indicates that they were the desired primary bromides, not rearranged secondary or tertiary bromides.[10] The structure of (V) was established by converting it, by carbonation of its Grignard reagent, to the corresponding carboxylic acid, the benzylamine salt of which was shown to be identical with that of *β*-phenyl-*n*-valeric acid prepared in two other ways. The reactions may be represented as



The structure of the olefins obtained on treatment of the bromides, (IV) and (V), with potassium amide in liquid ammonia was established by ozonization, by oxidation with chromic anhydride, or by oxidation with hydrogen peroxide in the presence of catalytic amounts of osmium tetroxide.[11] The aromatic portion of olefins of type (II) yielded acetophenone or propiophenone, which was isolated as the semicarbazone, while the aromatic portions of olefins of type (III) yielded benzaldehyde which in the ozonization or chromic anhydride treatment was ozidized to benzoic acid. In the hydrogen peroxide–osmium tetroxide treatment benzaldehyde was obtained, necessitating the development of a suitable procedure for separating it from the ketones. It was found possible to precipitate the ketone as the semicarbazone without precipitating the benzaldehyde (which was always present in relatively small amounts), and to precipitate the benzaldehyde as the semioxamazone[12] without precipitating the relatively larger amounts of ketone.

In Table I are given the data for typical experiments together with the yields of aromatic ketone and benzaldehyde or benzoic acid obtained by the oxidations of the olefinic products. While the reaction of 2-phenyl-1-bromobutane in the presence of less than an equivalent of potassium amide (experiments 5 and 6) gave the expected ketone, propiophenone, the reaction of this bromide with an excess of potassium amide (experiments 3 and 4) yielded acetophenone. The formation of the latter is explained on the basis of the prototropic change of the olefin, 2-phenylbutene-1, which was presumably first formed, to 2-phenylbutene-2, the change being effected by the base.



$$C_6H_5{-}\underset{\underset{CH_2}{\|}}{C}{-}CH_2{-}CH_3 \longrightarrow C_6H_5{-}\underset{\underset{CH_3}{|}}{C}{=}CH{-}CH_3$$

Also, it has been shown that when a portion of the olefinic product obtained in experiment (6), which evidently consisted mainly of a mixture of 2-phenylbutene-1 and 2-phenylbutene-2, was treated with excess potassium amide, the former olefin must have been converted to the latter since the resulting olefinic product on oxidation yielded acetophenone but no propiophenone.

It can be seen from Table I that in all cases the yields of aromatic ketone are much higher than those of benzaldehyde or benzoic acid, the yields of ketone apparently being relatively greater in the experiments with 2-phenyl-1-bromopropane. In experiment (1) with this bromide the ratio of ketone to benzoic acid is 32:1, while in experiment (2) ketone but no benzaldehyde was obtained. In experiment (3) with 2-phenyl-1-bromobutane the ratio of ketone to benzaldehyde is 16:1. In experiments (4) and (5), a portion of the ketone formed was doubtless oxidized by the chromic anhydride to benzoic acid, since blank experiments with an authentic sample of 2-phenylpropylene and with propiophenone gave 5% yields of benzoic acid. If this is taken into account the ratio of acetophenone to benzoic acid in experiment (4) would be at least 16:1, while in experiment (5), in which excess bromide was used, the ratio of propiophenone to benzoic acid would also be high.

From these results it may be concluded that the action of potassium amide on both 2-phenyl-1-bromopropane and 2-phenyl-1-bromobutane produced practically entirely olefins of type (II). The relatively low yields of rearranged olefins (III), which are indicated by the above results, might be accounted for on the basis that there occurred some *α*-elimination accompanied by rearrangement of the carbon skeleton (see note 8)

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[10] See Levene and Marker, *J. Biol. Chem.*, **108**, 409 (1935).

[11] Criegee and Richter, *Ann.*, **522**, 94 (1936).

[12] Kerp and Unger, *Ber.*, **30**, 565 (1897).

TABLE I

REACTION OF β-PHENYL SUBSTITUTED ALKYL BROMIDES WITH POTASSIUM AMIDE IN LIQUID AMMONIA

Expt.	Bromopropane	G.	Mole	Ether, ml.	KNH_2, mole[j]	Liquid NH_3, ml.	Time, min.	Olefinic product	Oxidizing reagent	Oxidation products[k] Ketone	%	Aldehyde or acid	%
1	2-Phenyl-1-	6.75	0.0339	..	0.051	200	60	3.50 g.[a]	O_3	Acetophenone	54	Benzoic acid	1.7
2	2-Phenyl-1-			..	Excess	...	...	61–63° (9 mm.)[b]	H_2O_2 (OsO_4)	Acetophenone		Benzaldehyde	0.0
3	2-Phenyl-1-	5.51	.0259	50	0.063	200	40	1.95 g.[c] 65° (9 mm.)	H_2O_2 (OsO_4)	Acetophenone	61	Benzaldehyde	3.8[d]
	Bromobutane												
4	2-Phenyl-1-	8.15	.0382	20	.059	225	150	4.92 g.[a]	CrO_3	Acetophenone	47	Benzoic acid	5.2
5	2-Phenyl-1-	6.50	.0305	20	.028	110	30	3.80 g.[e]	CrO_3	Propiophenone	50	Benzoic acid	8.7[f]
6	2-Phenyl-1-	6.0	.0280	50	.013	200	120	1.6 g.[g,h] 65–75° (8 mm.)	H_2O_2 (OsO_4)	Propiophenone and acetophenone[i]		Benzaldehyde	4[d]

[a] Halogen analysis indicated that olefinic product contained 1% unchanged bromide. [b] The olefinic product had stood in ether solution for one month before distillation; a residue of brown polymers remained in the flask. [c] A smaller fraction (0.73 g.) boiling at 155° (5 mm.) was also obtained; presumably this is a dimeric phenylbutylene. [d] Isolated as semioxamazone, m. p. 275°. [e] Halogen analysis indicated that the olefinic product contained 22% of the unchanged bromide. [f] A liquid acid, apparently phenylethylacetic acid, was also obtained in 4.8% yield; this could have resulted from the oxidation of 2-phenyl-1-bromobutane present in the olefinic mixture; see note (e). [g] Also, 2.4 g. of the original bromide (identified by its refractive index) was recovered. [h] Treatment of a portion (0.66 g.) of this olefinic mixture with excess potassium amide in liquid ammonia for one and one-half hours yielded an olefinic product, which, on oxidation, gave acetophenone (identified by the semicarbazone) but apparently no propiophenone. [i] The ketonic fraction yielded semicarbazone crystals melting at 161–168°, and was therefore assumed to be a mixture of acetophenone and propiophenone. [j] The moles of potassium amide were assumed to be equivalent to those of the metallic potassium used. [k] See experimental for definitions of yield.

or that the bromides were not entirely pure. In view of the tendency to rearrangement that compounds of type (I) exhibit with acidic reagents, it is possible that a little rearranged bromide was formed during the conversion of the alcohol to bromide and escaped detection in the proof of structure. Also, since bromide (IV) was prepared from phenylacetonitrile, the bromide might have been contaminated with a small amount of β-phenethyl bromide, which with potassium amide should form styrene from which benzaldehyde or benzoic acid would be obtained on oxidation.

Somewhat in contrast to Amagat's results with sodium amide[4] we have obtained approximately equal amounts of 2-phenylbutene-1 and 1-phenylbutene-1 (olefins of types II and III, respectively) when 2-phenyl-1-bromobutane was refluxed in xylene with a suspension of potassium amide. Also a considerable amount of bromide (either the original or a rearranged bromide) remained undecomposed by the potassium amide even after the reaction mixture had been refluxed for six hours. Although some of the 1-phenylbutene-1 might have been formed by action of the base on 2-phenyl-1-bromobutane (involving α-elimination of hydrogen bromide)[8] it seems likely that at least most of this olefin resulted from the rearranged bromides which could have been formed by a thermal rearrangement. When 2-phenyl-1-bromobutane was refluxed in xylene with a suspension of potassium carbonate some rearranged bromide was evidently formed since after treatment of the resulting bromide with potassium amide in liquid ammonia and oxidation of the olefinic product, three times the amount of benzoic acid obtained in experiment (4) was isolated.

Experimental

Phenylethylacetamide.—Phenylethylacetic acid (Eastman) was converted to the acid chloride by refluxing the acid with excess thionyl chloride in benzene solution, and removing the solvent and excess reagent by distillation *in vacuo*. The crude acid chloride was converted to the amide by pouring it into cold concentrated ammonium hydroxide. The crude amide was recrystallized from a mixture of ethyl ether and petroleum ether (b. p. 30–60°) giving a product melting at 83–84° (reported m. p. 83°)[3]; yield of pure amide, 75%.

2-Phenylbutanol-1.—Phenylethylacetamide (78 g., 0.48 mole) was dissolved in a 1-liter of absolute alcohol and poured into 132 g. (5.7 mole) of clean sodium (cut in 0.25 inch cubes) in a 5-liter 3-necked flask. After the vigorous initial reaction had subsided the mixture was refluxed for two hours. The excess sodium was decomposed by the cautious addition of a little water. After distilling off part of the alcohol the mixture was diluted with 0.5 liter of water and extracted with four 125-ml. portions of ether. The ether solution was washed with 5 *N* hydrochloric acid, 3 *N* sodium hydroxide and twice with water and then dried over "Drierite." Distillation at 18 mm. yielded 53.8 g. (75%) of colorless 2-phenylbutanol-1, boiling at 122–123° (reported b. p. 120–121° (18 mm.)).[3]

2-Phenyl-1-bromobutane.—This bromide was prepared essentially by the method of Levene, Marker and Rothen.[13] Phosphorus tribromide (17.4 ml., 0.2 mole) was added slowly to 20 g. of 2-phenylbutanol-1 cooled in an ice-bath. After standing overnight the mixture was heated on the water-bath for one hour and poured onto crushed ice. The resulting mixture was extracted with 150 ml. of petroleum ether (b. p. 30–60°). The petroleum ether solution of the bromide was extracted several times with 5% sodium carbonate solution, then once with cold concentrated sulfuric acid, again with sodium carbonate solution and finally with water. After drying with "Drierite" the solvent was removed and the bromide distilled at 1 mm. in an apparatus having a uniform 7-mm. internal diameter and a 3-cm. vapor path from the thermometer bulb to the condenser. With the bath temperature at 110–115°, the bromide boiled at 59–60° (reported b. p. 87° (1 mm.))[13]; n^{25}_D 1.5385; yield, 70%.

Anal. Calcd. for $C_{10}H_{13}Br$: Br, 37.50. Found: Br, 37.69.

Phenylmethylacetamide.—This compound was prepared by the methylation of phenylacetonitrile and the subsequent hydrolysis of the resulting phenylmethylacetonitrile to phenylmethylacetic acid which was converted to the amide through the acid chloride. The

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(13) Levene, Marker and Rothen, *J. Biol. Chem.*, **100**, 589 (1933).

methylation of the phenylacetonitrile was generally carried out using sodium[14] or sodium amide, but the phenylmethylacetamide obtained was contaminated with phenylacetamide (m. p., 154°) and usually several recrystallizations were required to obtain the phenylmethylacetamide melting at 91.5–92.5° (reported m. p. 91–92°).[3]

After the work was practically complete, it was found that purer phenylmethylacetamide could be obtained by titrating an ether solution of sodium triphenylmethide[15] with phenylacetonitrile (the end-point being indicated by the disappearance of the red color), methylating the sodium salt with excess methyl iodide, and hydrolysis of the phenylmethylacetonitrile. The phenylmethylacetamide thus obtained melted at 95.5°, which was not changed by several recrystallizations from water or a mixture of benzene and ligroin.

2-Phenyl-1-bromopropane.—This bromide was prepared from phenylmethylacetamide according to the procedure described above for the preparation of 2-phenyl-1-bromobutane. On reduction the amide yielded 2-phenylpropanol-1, boiling at 104.5–106.0° at 10 mm. (reported b. p., 112–114° (12 mm.)).[13] On treatment with phosphorus tribromide the alcohol yielded 2-phenyl-1-bromopropane, boiling at 73–74° at 1.5–2.0 mm. (reported b. p., 78° (1 mm.)).[13]

Anal. Calcd. for $C_9H_{11}Br$: Br, 40.16. Found: Br, 39.99.

Proof of Structure of 2-Phenyl-1-bromobutane.—The bromide (1,02 g.) in 25 ml. of ether was converted to the Grignard reagent by shaking it with 0.116 g. of magnesium for twelve hours in a glass-stoppered flask. The Grignard reagent on carbonation with Dry Ice, and hydrolysis with dilute sulfuric acid, yielded 0.493 g. (58%) of a colorless acid which solidified on standing; m. p. 50–51°. A solution of 50 mg. of the acid in 15 ml. of purified ligroin (b. p. 82–90°) was treated at the boiling point with 32 mg. (0.033 ml.) of benzylamine. On cooling the salt crystallized in fine, long threads; yield, 72 mg. (90%). After crystallization from ligroin (b. p., 82–90°) the salt melted at 109° and this melting point was not depressed by admixture with the benzylamine salt of β-phenyl-*n*-valeric acid prepared as described below.

Refluxing 1-phenylpropyl chloride and the sodium enolate of malonic ester in absolute alcohol gave diethyl α-phenylpropylmalonate, boiling at 160° at 11 mm.; n^{22}_D 1.4849. This substance on hydrolysis with alcoholic potassium hydroxide, and decarboxylation by boiling with dilute sulfuric acid, yielded β-phenyl-*n*-valeric acid, boiling at 140–141° at 4 mm., and melting at 59–60°. A sample of β-phenyl-*n*-valeric acid (m. p. 59–60°) was also prepared by the method of Reynolds[16] from benzalmalonic ester and ethylmagnesium bromide, followed by hydrolysis and decarboxylation. Both of these samples of β-phenyl-*n*-valeric acid yielded the benzylamine salt which, after one recrystallization, melted at 109.0–109.7°.

Reactions of Bromides with Potassium Amide in Liquid Ammonia. General Procedure.—The reactions were carried out in a transparent Dewar flask equipped with a stirrer and a dropping funnel. Commercial liquid ammonia was distilled from sodium and condensed into the reaction Dewar (protected from atmospheric moisture). Clean potassium and a small strip of rusty iron gauze were added to the ammonia and the blue solution stirred until colorless. This generally required thirty–forty minutes for 4 g. of potassium in 100 ml. of ammonia. To the vigorously stirred solution of potassium amide was added rapidly a solution of the bromide in anhydrous ether. The mixture acquired a dark red color which disappeared within a few minutes when excess of the bromide was used; the color persisted when excess of the potassium amide was present. After the desired time the solvents were allowed to evaporate, in certain cases the reaction being first stopped by the cautious addition of several drops of water. The residue was shaken with water and ether. The ether solution was extracted with dilute phosphoric or hydrochloric acid solution (from which less than 1% of amine was obtained) and again with water. After drying over "Drierite" the ether solution was evaporated, yielding the neutral olefinic product which was analyzed by the oxidation methods described below; in certain cases the olefin was distilled. Data for typical experiments are summarized in Table I.

Analysis of Olefinic Products. (a) Ozonization.—The olefinic product was dissolved in ten times its weight of pure glacial acetic acid and treated with washed ozone (7% by volume, flowing at the rate of 10 liters per hour) for two hours at room temperature. After refluxing for one hour the mixture was cooled, made basic with cold concentrated sodium hydroxide solution, and extracted three times with ether. Evaporation of the dried ether extracts yielded ketone which was converted to semicarbazone; washing the latter with petroleum ether and evaporation of the solvent yielded some unchanged olefin. Acidification of the alkaline solution and extraction with ether yielded, on evaporation of the solvent, benzoic acid contaminated with a little acetic acid; the latter was dissolved in a little water, a solubility correction being made for the solubility of the benzoic acid.

(b) **Oxidation with Chromic Anhydride.**—The olefinic product was dissolved in six to ten times its volume of pure glacial acetic acid. The calculated amount of chromic anhydride was added in small portions, maintaining the temperature at 60–65° until the mixture assumed a bright green color. The mixture was diluted with ten times its volume of water, extracted five times with ether, and the combined ether extracts washed with water. The acidic oxidation products were extracted from the ether with 3 *N* sodium hydroxide (and isolated in the usual manner) while the neutral oxidation products were obtained from the washed and dried ether solution. The ketone was converted to semicarbazone, some unchanged olefin generally being recovered.

(c) **Oxidation with Hydrogen Peroxide and Osmium Tetroxide.**—The olefinic product was added to an ethyl ether solution of hydrogen peroxide and osmium tetroxide[11] and the mixture allowed to stand at room temperature until colorless. Several extractions with water removed from the ether, hydrogen peroxide and any formaldehyde and acetaldehyde present. The remaining ether solution, generally containing only a small amount of benzaldehyde and a relatively larger amount of acetophenone, was divided into two equal parts and each evaporated through an eight inch straight tube column, special care being taken to avoid losses by "creeping." One of the residues was shaken for two hours in a glass-stoppered flask with an aqueous solution containing an excess of semicarbazide hydrochloride and sodium acetate. In this manner the acetophenone was precipitated as the semicarbazone (solubility, 0.014 g. per 100 g. of water) leaving the benzaldehyde semicarbazone in solution. The other residue was shaken with an aqueous solution containing an excess (based on the benzaldehyde) of semioxamazide, yielding a precipitate of benzaldehyde semioxamazone (solubility, 0.012 g. per 100 g. of water) and leaving acetophenone semioxamazone (solubility >1.0 g. per 100 g. of water) in solution, care being taken to prevent air oxidation of the benzaldehyde. The resulting mixtures from these two reactions were slightly yellow but, on filtering, white precipitates of the derivatives were obtained; the yields given in Table I include a solubility correction.

The products obtained in methods (a), (b) and (c) were identified by their melting points and mixed melting points with authentic specimens. When methods (a) and (b) were used the yields of products given in Table I were based on the amount of olefin used minus that recovered.

Reaction of 2-Phenyl-1-bromobutane with Potassium Amide in Boiling Xylene.—A sample of 2-phenyl-1-bromobutane was refluxed in purified xylene with a suspension of excess (freshly prepared) potassium amide. After three hours, one-half of the mixture was removed with a pipet, and the remainder heated for three hours longer. The two portions were separately diluted with

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(14) Baldinger and Nieuwland, This Journal, **55**, 2853 (1933).

(15) See Hudson and Hauser, *ibid.*, **63**, 3156 (1941).

(16) Reynolds, *Am. Chem. J.*, **44**, 315 (1910).

ether and extracted with water, dilute hydrochloride acid, dilute sodium hydroxide and finally with water. The dried xylene–ether solutions were distilled and the residues fractionated. The residue from the three-hour treatment yielded an olefinic product (b. p., 80–95° at 20 mm.) and approximately twice as much undecomposed bromide, while the residue from the six-hour treatment yielded an olefinic product (b. p. 85–95° at 20 mm.), an analysis of which indicated the presence of 25% bromide. Oxidation of the former olefinic product with chromic anhydride (method b) gave approximately 25% yields each of propiophenone and benzoic acid while oxidation of the latter olefinic product gave 25 and 30% yields of propiophenone and benzoic acid, respectively.

Treatment of 2-Phenyl-1-bromobutane with Potassium Carbonate in Boiling Xylene.—A sample of 2-phenyl-1-bromobutane (which did not give an immediate precipitate with alcoholic silver nitrate) was refluxed for fifteen hours in purified xylene with a suspension of excess potassium carbonate. The solvent was distilled and a bromide (which gave an immediate precipitate with alcoholic silver nitrate) was recovered boiling at 120–125° at 20 mm. No lower boiling product was found. The recovered bromide on treatment with excess potassium amide in liquid ammonia yielded an olefinic product which on oxidation with chromic anhydride (method b) gave a 33% yield of acetophenone and a 16% yield of benzoic acid.

Summary

1. It has been shown that 2-phenyl-1-bromopropane and 2-phenyl-1-bromobutane react with potassium amide in liquid ammonia to form largely unrearranged olefins.

2. In the presence of excess potassium amide in liquid ammonia, 2-phenylbutene-1 undergoes a prototropic change to form 2-phenylbutene-2.

3. When 2-phenyl-1-bromobutane is refluxed in xylene with potassium amide approximately equal amounts of unrearranged and rearranged olefins are obtained.

4. When 2-phenyl-1-bromobutane is refluxed in xylene with potassium carbonate a portion of the bromide apparently undergoes rearrangement.

DURHAM, N. C. RECEIVED OCTOBER 7, 1946

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, CARBIDE AND CARBON CHEMICALS CORP.]

Deoxygenation of Certain Aldehydes and Ketones: Preparation of Butadiene and Styrene[1]

BY W. M. QUATTLEBAUM, W. J. TOUSSAINT AND J. T. DUNN

This paper reports some of the basic experimental work on the process used during the recent emergency for the manufacture of butadiene from ethanol; a common mechanism is proposed for the various syntheses of butadiene from ethanol; and a related synthesis for styrene is described.

For many years prior to the work reported here, it was known that butadiene could be made in low yield by passing ethanol over powdered aluminum metal,[2] or in fair yields from ethanol and acetaldehyde over an alumina or clay catalyst,[3] and from ethanol alone over a combined dehydrating and dehydrogenating catalyst.[4]

While the yields obtained in the latter two processes represented a marked improvement over those reported by Ipatiev, they were still low, and the butadiene was contaminated with at least 15% of butylenes.

At the outset of the present program it seemed reasonable to suppose that the efficiency of the Ostromisslensky process, and the quality of the resulting butadiene, might both be improved, if the reactions responsible for the formation of four-carbon material from two-carbon material could be determined. With this in mind, an investigation into the mechanism of the reaction was undertaken. This work led to the conclusion that the deoxygenation of crotonaldehyde is responsible for the formation of butadiene in the Ostromisslensky reaction. It also resulted in an extension of the deoxygenation reaction to certain other aldehydes and ketones.

Deoxygenation of Crotonaldehyde by Ethanol. Ostromisslensky[3] and later Maximoff[5] obtained butadiene from diethyl acetal, ethyl vinyl ether, acetaldol, crotonaldehyde, tetrahydrofuran, etc. These compounds, however, were investigated only as potential commercial sources of butadiene, and not as possible intermediates in the acetaldehyde–ethanol reaction. Indeed Ostromisslensky came to the conclusion that 1,3-butylene glycol was the intermediate from which the butadiene was formed, and that the butylene glycol was derived from an acetaldehyde–ethanol hemiacetal as follows

$$H_3CCH(OH)OC_2H_5 \longrightarrow H_3CCH(OH)CH_2CH_2OH$$

To prove that it was the methyl group, and not the methylene group of ethanol, which combined with the carbon of the aldehyde carbonyl group, Ostromisslensky adduced the evidence that substitution of *i*-propanol for ethanol led to the formation of piperlylene

$$\begin{aligned}&CH_3CHO + CH_3CH(OH)CH_3 \longrightarrow\\&\qquad CH_3CH(OH)CH_2CH(OH)CH_3 \longrightarrow\\&\qquad\qquad CH_3CH{=}CHCH{=}CH_2 + 2H_2O\end{aligned}$$

instead of isoprene

$$\begin{aligned}&CH_3CHO + CH_3CH(OH)CH_3 \longrightarrow\\&\qquad CH_3CH(OH)C(CH_3)_2OH \longrightarrow\\&\qquad\qquad H_2C{=}CHC(CH_3){=}CH_2 + 2H_2O\end{aligned}$$

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[1] Publication of this paper has been withheld since 1942 because of Government secrecy orders.

[2] Ipatiev, *J. prakt. Chem.*, **2**, 67 (1903).

[3] Ostromisslensky, *J. Russ. Phys.-Chem. Soc.*, **47**, 1472–1506, 1491 (1915).

[4] Lebedev, British Patent 331,402.

[5] Maximoff, U. S. Patent 1,682,919.