Anal. Calcd. for $C_{12}H_{13}AsN_2O_6$: As, 21.03. Found: As, 21.08, 21.01.

1-(*p*-Arsonophenyl)-3-carboxy-4-hydroxypyrazole (XVI).—A portion of XV (2.3 g., 0.0065 mole) was refluxed for four hours in 25 ml. of water containing sodium hydroxide (0.8 g., 0.02 mole). The solution was treated with charcoal, filtered and acidified to congo red paper. The yellow solid that separated was filtered off and dried at 80°; yield 1.7 g. (80%). Attempted decarboxylations were unsuccessful.

Anal. Calcd. for $C_{10}H_9AsN_2O_6$: As, 22.83. Found: As, 22.72, 22.87.

1-(*p*-Arsonophenyl)-3-carbethoxy-4-hydroxy-5-bromopyrazole (XVII).—Compound XIII (10.0 g., 0.028 mole) was dissolved by warming in 100 ml. of glacial acetic acid containing sodium acetate (7.0 g., 0.09 mole). While the solution was stirred mechanically, bromine (9.0 g., 0.056 mole) in 10 ml. of acetic acid was added over a period of fifteen minutes, the temperature ranging from 30–40°. The reaction mixture was poured into water and the yellow product that separated was filtered off and recrystallized from an acetone–water mixed solvent. The analysis indicated that the pyrazole had been formed completely in the reaction mixture.

Anal. Calcd. for $C_{12}H_{12}AsBrN_2O_6$: As, 17.22. Found: As, 17.00, 17.12.

Ethyl α-Chloroglyoxylate-*p*-arsonophenylhydrazone (XVIII).—Ethyl α-chloroacetoacetate was prepared by the method of Michael and Carlson.[10] *p*-Arsanilic acid (13.7 g., 0.06 mole) was dissolved in 100 ml. of water containing sodium hydroxide (2.6 g., 0.06 mole). The solution was cooled and a solution of sodium nitrite (4.5 g., 0.06 mole) in 50 ml. of water was added. This solution was poured into a mixture of ice and 14.4 ml. of concentrated hydrochloric acid and the resulting diazonium solution was added rapidly to a solution of ethyl α-chloroacetoacetate (10. g., 0.06 mole) in 200 ml. of ethyl alcohol containing sodium acetate (5.0 g., 0.06 mole). The mixture was stirred mechanically and cooled in an ice–salt-bath for two hours, then allowed to stand for twelve hours at room temperature. The yellow product was filtered off and recrystallized from ethyl alcohol; yield 7.1 g. (34%).

Anal. Calcd. for $C_{10}H_{12}AsClN_2O_5$: C, 34.26; H, 3.45; As, 21.37. Found: C, 34.41, 34.53; H, 3.71, 3.68; As, 21.42, 21.32.

(10) Michael and Carlson, THIS JOURNAL, **58**, 353 (1936).

Summary

A new method of synthesis for phenyl-1,2,4-triazole derivatives has been developed and a number of arsenic-containing and arsenic-free heterocyclic compounds of this type have been prepared.

A number of glyoxylic acid *p*-arsonophenylhydrazone derivatives have been synthesized and from several of these some *p*-arsonophenyl-4-hydroxypyrazole compounds have been made.

LINCOLN, NEBRASKA RECEIVED DECEMBER 14, 1945

[CONTRIBUTION FROM THE WELLCOME RESEARCH LABORATORIES]

Amines Related to 2,5-Dimethoxyphenethylamine. III[1] 2-Hydroxy and 2-Methoxy-5-methylphenylalkanolamines

BY ALAN E. ARDIS,[2] RICHARD BALTZLY AND WILLIAM SCHOEN

Pharmacological studies of the substances reported in the earlier papers of this series[3] having shown that considerable value as pressors is exhibited by the primary and secondary β-hydroxy-β-(2,5-dimethoxy)-phenylethyl and phenylisopropylamines, it was of interest to compare these with the analogous substances in which the 5-methoxyl group was exchanged for a methyl group. At the same time the preparation of 2-hydroxy-5-methyl analogs by using the benzyl group for protection proved to be feasible although offering some experimental difficulties in the earlier part of the work.

The general course of the reactions is indicated in the chart. The primary isopropylamines were prepared from the corresponding oximino ketones. The synthesis of the other members of the series was through the α-bromoketones; the primary amines being made by the hexamethylenetetramine method, the secondary by the benzylmethylamine procedure.

Certain difficulties, in part unanticipated, were encountered. The chief of these was dealkylation in the preparation of the necessary α-bromoketones. Whereas 2,5-dimethoxyacetophenone on bromination in chloroform solution yields readily the desired 2,5-dimethoxy-α-bromoacetophenone, and 2,5-dimethoxy-α-bromopropiophenone is easily obtained in usable form,[4] the 2-methoxy ketones of the present series by the chloroform bromination gave the α-bromoketones in poor yield or not at all. This was probably due to unfavorable physical properties. When the 2-benzyloxyketones were brominated, dealkylation was extensive and accompanied by ring bromination. The crude preparations so obtained sufficed in certain cases for the preparation of secondary amines, but could not be used with the hexamethylenetetramine method. Bromination in

(1) This work is part of a joint research being carried out in collaboration with a pharmacological group in the same laboratories.

(2) Present address: Research Laboratory, The B. F. Goodrich Company, Akron, Ohio.

(3) Baltzly and Buck, THIS JOURNAL, **62**, 161, 164 (1940). The pharmacological reports on these substances are now in the process of preparation and should appear soon. Briefly, the primary and secondary bases of the phenylethyl and phenylisopropylamine types have been found to possess potency rather surprising in pressors with methoxyl rather than hydroxyl groups on the rings. The activity of the phenylalkanolamines is considerably greater than that of the bases with no hydroxyl beta to the nitrogen atom,

(4) The second paper of this series describes the preparation and synthetic use of this substance. Sometime after the date of publication, an oily sample in the refrigerator solidified. Opportunity is taken in the experimental section to characterize it further.

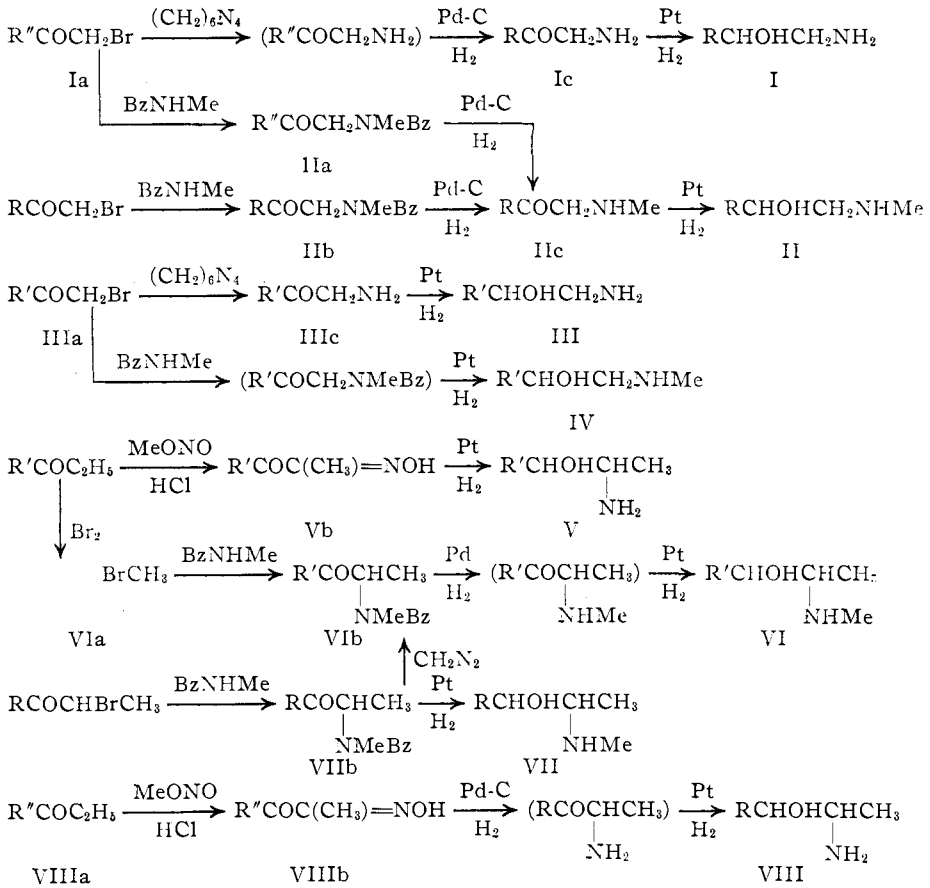


CHART I.—Bz = benzyl; R = 2-hydroxy-5-methylphenyl; R′ = 2-methoxy-5-methylphenyl; R″ = 2-benzyloxy-5-methylphenyl.

carbon tetrachloride solution[5] was still less satisfactory but a suitable brominating solvent was eventually found in methanol. In this solvent even the 2-benzyloxy ketones could be brominated with the formation of no more than traces of 2-hydroxy compound (as judged by the ferric chloride test). Even with the use of homogeneous α-bromoketones three of the four tertiary aminoketones resulting from the reactions with benzylmethylamine were not obtained crystalline although pure enough for catalytic reduction to the final products or isolable intermediates.

Two other methods were explored in attempts to prepare β-hydroxy-β-(2-hydroxy-5-methylphenyl)-ethylamine (III). The reaction of 2-benzyloxy-5-methyl-α-bromoacetophenone with potassium phthalimide gave the desired phthalimido derivative in good yield but it was neither feasible to reduce this before hydrolysis nor before reduction to hydrolyze it so as to obtain a workable product. Failure similarly attended an attempt to utilize the Schroeter adaptation[6] of the Curtius rearrangement. The hydrazide of β-(2-benzyloxy-5-methylphenyl)-hydracrylic acid was prepared without trouble but the next stage of the reaction gave negligible yields, probably due to the insolubility of the hydrazide (and perhaps also of the azide).

It had originally been intended to prepare from the phenolic alkanolamines of this type the carbethoxyl[7] and ethyl carbamato derivatives. This plan was abandoned after the most promising lines of attack had failed. The carbethoxylation of the 2-hydroxyketones was accomplished only by a reaction of the anhydrous sodium salt with ethyl chlorocarbonate. When introduced at this point the ester grouping did not survive the subsequent reactions. Attempts to carbethoxylate the *o*-hydroxy tertiary aminoketones were unsuccessful.

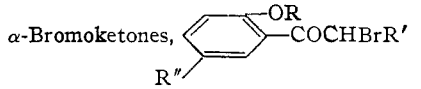
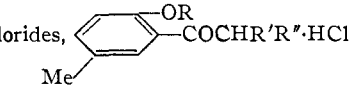
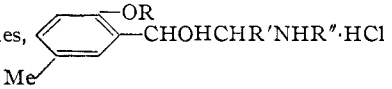
In a similar fashion the *o*-hydroxy tertiary aminoketones resisted the action of ethyl isocyanate even at reflux temperatures. As model experiments on catechol bis-ethylcarbamate had shown this grouping to be sensitive to bases

(5) Addition of bromine to solutions of these ketones in carbon tetrachloride was accompanied by very little evolution of hydrogen bromide and by the precipitation of dark reddish-brown solids which could not be purified and tended to give up hydrogen bromide when evacuated. Presumably these were enol dibromides, usually postulated as intermediates in the halogenation of ketones.

(6) Schroeter, German Patent 220,852; *cf.* also Paper II of this series.

(7) *Cf.* Buck and Baltzly, THIS JOURNAL, **64**, 2263 (1942).

TABLE I

R	R′	R″	Chart no.	Crystallizing solvent[a]	Appearance[b]	M. p., °C.	Empirical formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
α-Bromoketones, 											
Me—	Me—	MeO—		P	Plates	49–49.5	$C_{11}H_{13}O_3Br$	48.36	4.80	48.34	5.07
Bz—	H—	Me—	Ia	Æ-H	Needles	85–85.5	$C_{16}H_{15}O_2Br$	60.19	4.74	59.95	4.60
Me—	Me—	Me—	VIa	P		17	$C_{11}H_{13}O_2Br$	51.37	5.10	51.23	5.20
Bz—	Me—	Me—		Æ-H	Prisms	58.5–59.5	$C_{17}H_{17}O_2Br$	61.24	5.15	61.04	5.18
α-Aminoketone hydrochlorides, 											
Me—	—H	—NH_2	IIIc	A	Needles	201.5–203 (dec.)	$C_{10}H_{14}O_2NCl$	55.67	6.54	55.87	6.43
H—	—H	—NH_2	Ic	A	Pale yellow rhombs	222–225 (dec.)	$C_9H_{12}O_2NCl$	53.57	6.00	53.52	6.15
Bz—	—H	—NMeBz	IIa	A-E	Needles	154–156	$C_{24}H_{26}O_2NCl$	72.79	6.62	73.00	6.51
H—	—H	—NMeBz	IIb	A-E-Æ	Silky needles	186.5–187	$C_{17}H_{20}O_2NCl$	66.75	6.60	66.53	6.52
H—	—H	—NHMe	IIc	A-Æ	Prisms	204–206	$C_{10}H_{14}O_2NCl$	55.67	6.54	55.88	6.72
H—	—Me	—NMeBz	VIIb	A-E-Æ		185–186	$C_{18}H_{22}O_2NCl$	67.60	6.94	67.36	7.15
Me—	—Me	—NMeBz	VIb	A-E	Leaflets	211.5–213.5	$C_{19}H_{24}O_2NCl$	68.32	7.25	68.13	7.67
Aminoalcohol hydrochlorides, 											
Me—	—H	—H	III	A-E-Æ	Needles	144–145	$C_{10}H_{16}O_2NCl$	55.14	7.41	55.08	7.34
H—	—H	—H	I	A-E-Æ	Needles	144–144.5	$C_9H_{14}O_2NCl$	53.05	6.93	53.00	6.70
Me—	—Me	—H	V	A-E	Fine needles	218 (dec.)	$C_{11}H_{18}C_2NCl$	57.00	7.83	57.18	7.69
H—	—Me	—H	VIII	A-E	Small prisms	214–214.5	$C_{10}H_{16}O_2NCl$	55.14	7.41	54.93	7.33
Me—	—H	—Me	IV	A-E	Prisms	167.5–168.5	$C_{11}H_{18}O_2NCl$	57.00	7.83	56.98	7.97
H—	—H (acid oxalate)	—Me	II	Ac-Aq-E		151	$C_{12}H_{17}O_6N$	53.11	6.32	53.08	6.20
Me—	—Me	—Me	VI	A-E	Hexagonal prisms	186–187	$C_{12}H_{20}O_2NCl$	58.63	8.21	58.95	8.27
H—	—Me	—Me	VII	A-E		197.5–198	$C_{11}H_{18}O_2NCl$	57.00	7.83	56.94	7.98
4-Ethylcarbamatophenyl derivatives $EtNHCOOC_6H_4$—R											
—CHO			IXa	E		90–92	$C_{10}H_{11}O_3N$	62.14	5.74	62.43	5.90
—$CH_2CH_2NH_2$·HCl			IX	A-E		220 (dec.)	$C_{11}H_{17}O_2N_2Cl$	53.96	7.00	54.11	6.78
—CH_2CH_2NMeBz·HCl			Xa	A		199.5–200	$C_{19}H_{25}O_2N_2Cl$	65.37	7.23	65.51	7.29
—CH_2CH_2NHMe·HCl			X	A-Æ	Glossy platelets	208	$C_{12}H_{19}O_2N_2Cl$	55.69	7.41	55.85	7.78

[a] A = absolute ethanol, Æ = ethyl acetate, E = ether, H = hexane, P = pentane, Ac = acetone, Aq = water. [b] Appearance is noted only where crystal form is distinctive.

although very resistant to acids[8] this project was also judged unpromising. In exploratory experiments the O-ethyl carbamates of homo-anisylamine and N-methylhomoanisylamine were prepared. Details of the syntheses are included in the experimental section.

Experimental

Physical and analytical data on the α-bromoketones, the aminoalcohols and those α-aminoketones isolated in pure form are presented in Table I. All melting points are corrected.

Preparation of α-Bromoketones.—The starting ketones were dissolved in about five parts of methanol and the calculated amount of bromine was added gradually with stirring and occasional cooling. In most cases, a few drops of concd. hydrochloric acid was added initially. No significant differences were observed when the bromine was added directly or dissolved in cold methanol. The benzoxyacetophenone derivative Ia crystallized so rapidly during the bromination that stirring became impossible and it was necessary to filter off the solid and complete the bromination on the filtrate. The low-melting propiophenone VIa was crystallized only from pentane with Dry Ice cooling.

α-Benzylmethylaminoketones.—The appropriate α-bromoketones were dissolved in absolute ether and allowed to react at room temperature with two equivalents of benzylmethylamine for twenty-four–seventy-two hours. During this period the bulk of the excess secondary amine crystallized as the hydrobromide, and this was filtered off. The filtrate was allowed to stand two to three hours with an excess of acetic anhydride and the solution was then extracted with dilute hydrochloric acid. On evaporation of these acid solutions *in vacuo*, the tertiary aminoketone

(8) Catechol bis-ethylcarbamate can be recrystallized from concentrated hydrochloric acid,

hydrochlorides remained as sirupy residues, some of which could not be crystallized, but all of which were pure enough to be reduced catalytically. 2-Hydroxy-5-methyl-α-benzylmethylaminoacetophenone hydrochloride (IIb) was thus obtained from impure fractions of α-bromoketone prepared by the bromination in chloroform of 2-benzyloxy-5-methylacetophenone (b. p. (1 mm.) 171–172°). A somewhat purer specimen resulted when the α-halogenoketone fraction from a Fries rearrangement of *p*-cresol bromoacetate was used.[9] Both these specimens and the corresponding 2-benzyloxy compound (IIa) when hydrogenated with palladized charcoal, suffered debenzylation, yielding 2-hydroxy-5-methyl-α-methylaminoacetophenone hydrochloride (IIc).

2 - Hydroxy - 5 - methyl - α - benzylmethylaminopropiophenone (VIIb) (prepared from the known 2-hydroxy-5-methyl-α-bromopropiophenone) reacted slowly with diazomethane to give the 2-methoxy analog (VIb).[10]

α-Aminoketones.—The aminoketones needed for the preparation of the primary aminoalcohols I and III were obtained by the hexamethylenetetramine method. The reaction product from 2-benzyloxy-5-methyl-α-bromoacetophenone and hexamethylenetetramine, when decomposed in the usual way with alcoholic hydrogen chloride gave a product whose solubilities were so similar to those of ammonium chloride that the separation was laborious and incomplete. The purest sample obtained crystallized in needles, m. p. 191–192°, but was not free of inorganic material. The most profitable procedure proved to be to reduce the total precipitate from the alcoholysis with palladized charcoal in 95% alcohol. The hydrogen absorption was 85% of that calculated (from the starting bromoketone) and the 2-hydroxy aminoketone Ic was easily purified.

2-Methoxy-5-methyl-α-isonitrosopropiophenone (Vb).—This compound was prepared from 2-methoxy-5-methylpropiophenone by the methyl nitrite method of Hartung and Crossley.[11] It separated from ethyl acetate–hexane mixture in pale yellow crystals, m. p. 101.5–102°.

Anal. Calcd. for $C_{11}H_{13}O_3N$: C, 63.75; H, 6.33. Found: C, 63.94; H, 6.54.

2-Benzyloxy-5-methyl-α-isonitrosopropiophenone (VIIIb).—This substance was also prepared by the above method. It was crystallized from ethyl acetate–hexane mixture, m. p., 95.5°.

Anal. Calcd. for $C_{17}H_{17}O_3N$: C, 72.06; H, 6.05. Found: C, 71.82; H, 6.12.

Preparation of the Amino Alcohols.—In all cases the hydrogenation of amino ketones to amino alcohols was accomplished with a platinum (Adams) catalyst in alcoholic or aqueous solution. The isonitrosoketones (Vb and VIIIb) could be reduced either with platinum alone (one-step reduction) or successively with palladized charcoal followed by platinum. The latter procedure was employed in the preparation of compound VIII (without intermediate purification of the aminoketone) and is probably preferable as the isonitroso group is reduced more rapidly by this method. A similar two-step reduction without isolation of intermediate was employed in the passage from VIb to VI. One-step reductions with Adams catalyst were employed in the preparation of VII from VIIb and of IV from the non-crystalline reaction product of benzylmethylamine with 2-methoxy-5-methyl-α-bromoacetophenone.[12] As the hydrochloride of the secondary aminoalcohol II could not be induced to crystallize, the material was transformed to the acid oxalate which had more satisfactory physical characteristics.

4-Ethylcarbamatophenethylamines.—4-Ethylcarbamatophenethylamine was prepared by the method of Buck.[13] An excess of ethyl isocyanate was allowed to react in ethereal solution with *p*-hydroxybenzaldehyde. The urethan aldehyde (IXa) so obtained, was transformed to the cyanhydrin (m. p., 82°) which was hydrogenated in alcoholic hydrogen chloride with Adams catalyst, yielding IX.

The base liberated from a sample of 4-hydroxyphenethylbenzylmethylamine hydrochloride[7] was dried in ethereal solution over potassium carbonate and treated with an excess of ethyl isocyanate to give Xa. Reduction of Xa with palladized charcoal produced the secondary amine X.

2-Benyloxy-5-methylpropiophenone (VIIIa).—The benzylation of *o*-propionyl-*p*-cresol with benzyl chloride and potassium hydroxide was performed in methanol solution. A 50% excess of the reagents was employed, and a product giving a negative ferric chloride test was obtained in 84% yield. The substance boiled at 176–179° (3 mm.) and melted at 43°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.30; H, 7.10. Found: C, 80.28; H, 7.35.

2-Benzyloxy-5-methylbenzaldehyde.—The benzylation by the above technique of 2-hydroxy-5-methylbenzaldehyde gave the 2-benzyloxy aldehyde in 80% yield. It crystallizes from hexane in colorless needles, m. p. 58.5–59°, b. p. (1 mm.), 150–155°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.50; H, 6.34.

β-(2-Benzyloxy-5-methylphenyl)-hydracrylic Acid.—The above aldehyde was condensed with ethyl bromoacetate by the Reformatzky method, and the reaction mixture was saponified in the cold. The acid product crystallized from ether–hexane mixture as colorless felted needles, m. p., 120.5–121.5°.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.29; H, 6.34. Found: C, 71.60; H, 6.57.

β-(2-Benzyloxy-5-methylphenyl)-hydracrylic Acid Hydrazide.—The acid from the preceding preparation was esterified with an excess of diazomethane and the product was transformed to the hydrazide which crystallized in nodules of fine needles. Recrystallized from alcohol it melted at 179.5–180°.

Anal. Calcd. for $C_{17}H_{20}O_3N_2$: C, 67.95; H, 6.72. Found: C, 68.32; H, 6.85.

5-(2-Benzyloxy-5-methylphenyl)-oxazolidone-2.—Six grams of the hydrazide was subjected to the Curtius rearrangement. The greater part of the product was a high melting and insoluble substance whose structure has not been elucidated. The more soluble fraction weighed 1.5–2 g. and contained some of the desired oxazolidone together with considerable of the high-melting material. After four recrystallizations from benzene–hexane the oxazolidone was obtained as tiny, colorless needles, m. p., 150–150.5°.

Anal. Calcd. for $C_{17}H_{17}O_3N$: C, 72.05; H, 6.05. Found: C, 72.23; H, 6.06.

The experiment was repeated a number of times with variations of the conditions, but without improving the yield.

2-Benzyloxy-5-methylphenacyl Phthalimide.—This substance was prepared in excellent yield by refluxing 2-benzyloxy-5-methyl-α-bromoacetophenone with potassium phthalimide in xylene. It separated from alcohol as large, colorless prisms with a square cross-section, m. p., 150°.

(9) Wittig, Bargert and Richter, *Ann.*, **446**, 155 (1925) prepared α-bromo-2-hydroxy-5-methylacetophenone by this method and recorded its melting point as 45.5–46.5°. In our hands the reaction gave much tar but about 40% of the material could be obtained as a distillate boiling over a considerable range. The fractions of this distillate solidified; the higher-boiling melted as low as 53–55°, the lower-boiling as high as 60–61°. This suggests that halogen exchange had taken place and that the product was a mixture of chloro and bromo ketones. The analytical results were in agreement with this supposition.

(10) This is not necessarily inconsistent with the finding of Schönberg and Moubasher, *J. Chem. Soc.*, 366 (1944), that diazomethane does not react with *o*-hydroxyacetophenone. These *o*-hydroxy-α-aminoacetophenones give no color with ferric chloride and are very poorly extracted from ethereal solution by dilute alkali. Chelation appears to be weaker or different in kind from the type usual with *o*-hydroxyketones.

(11) Hartung and Crossley, "Organic Syntheses," **16**, 45 (1936).

(12) Krollpfeiffer and Schneider, *Ber.*, **61B**, 1284 (1928).

(13) Buck, THIS JOURNAL, **55**, 2593, 3388 (1933).

Anal. Calcd. for $C_{24}H_{19}O_4N$: C, 74.77; H, 4.97. Found: C, 74.71; H, 4.88.

Reductions with aluminum isopropylate, palladized charcoal and with platinum proved unsatisfactory due mainly to the insolubility of the starting material and its primary reduction products. Reductions with sodium and alcohol apparently produced some toluene, but no pure material could be isolated from the reduction mixtures.

Acknowledgment.—The authors wish to express their gratitude to Messrs. Walter S. Ide, James E. Murphy and Samuel W. Blackman for the microanalyses here reported.

Summary

The primary and secondary amino alcohols of the 2-hydroxy and 2-methoxy-5-methylphenethyl and phenylisopropylamine series have been prepared.

TUCKAHOE 7, NEW YORK RECEIVED OCTOBER 10, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Isomerization of Alkanes. I. Effect of Olefins upon the Isomerization of *n*-Butane in the Presence of Aluminum Halide–Hydrogen Halide Catalyst

BY HERMAN PINES AND R. C. WACKHER

The catalytic isomerization of butanes has been in the last few years, a subject of extensive study.[1]

The reactants and catalysts used in the experiments were not completely free of extraneous contaminants which are usually inherent in the reagents used or in the technique of operation.

Recently, Leighton and Heldman[2] and Heldman[3] have carried out the isomerization of *n*-butane under more careful experimental conditions, using high vacuum apparatus. These authors studied the kinetics of isomerization of butane and, in accordance with the observation of previous investigators,[1,4] found that aluminum bromide–hydrogen bromide is an effective isomerization catalyst.

An attempt to study the kinetics of butane isomerization was made by the present authors. The experiments were carried out in sealed tubes, using a high-vacuum technique for the purification of the reagents and for charging and discharging the products. This study had to be abandoned, however, because the results obtained were erratic owing to some impurities in *n*-butane which were not separated by fractional distillation. It was noticed that when apparently pure *n*-butane was further purified by passing it over aluminum chloride granules and then redistilled, no isomerization of this *n*-butane in the presence of aluminum bromide–hydrogen bromide took place.

It was found that in order to cause the isomerization of *n*-butane under relatively mild conditions it was necessary to add various compounds which are ordinarily present as impurities in the commercial butane isomerization processes. Olefins, air and water individually or collectively act as promoters for the isomerization of *n*-butane. These compounds may serve as a source of, or may cause the formation of, carbonium ions, which seem to be required to promote the isomerization of paraffins.

The present paper is limited to the effect of olefins upon the isomerization of *n*-paraffins; the effect of air and water upon this reaction will be discussed in succeeding papers of this series.

The addition of 0.01% of *n*-butenes to *n*-butane was sufficient to cause the isomerization of *n*-butane in the presence of aluminum chloride–hydrogen chloride at 100°. The effect of olefin concentration upon the isomerization of *n*-butane in the presence of aluminum bromide–hydrogen bromide and aluminum chloride–hydrogen chloride was studied. In the absence of olefins which may serve as a source of carbonium ions aluminum halide–hydrogen halide does not cause the isomerization of butane, unless the experimental conditions are conducive to the formation of decomposition products. This can be accomplished either by raising the temperature of reaction or by increasing the amount of hydrogen halide introduced. The data obtained in this investigation are not in agreement with the experimental results obtained by Heldman[3] who, most likely, did not purify the butane sufficiently to remove impurities which might act as a source of, or initiate the formation of, carbonium ions.[5]

Experimental

Materials.—Aluminum bromide was prepared by the action of bromine on aluminum foil in a stream of dry nitrogen. The product was partially purified by distillation in a stream of dry nitrogen and sealed into small, weighed ampoules according to the general method developed by A. Stock.[6] Final purification was carried out

(1) (a) C. W. Montgomery, J. H. McAteer and N. W. Franke, THIS JOURNAL, **59**, 1768 (1937); (b) G. C. A. Schuit, H. Hoog and J. Verheus, *Rec. Trav. Chim.*, **59**, 793 (1940); (c) B. Moldavskii and T. Nizovkina, *J. Gen. Chem., U. S. S. R.*, **9**, 1652 (1939); (d) C. W. Montgomery, J. H. McAteer and N. W. Franke, paper presented before the Petroleum Division of the American Chemical Society, April 3–7, 1939, Baltimore, Md.

(2) P. A. Leighton and J. D. Heldman, THIS JOURNAL, **65**, 2276 (1943).

(3) J. D. Heldman, *ibid.*, **66**, 1786 (1944).

(4) V. N. Ipatieff and H. Pines (to Universal Oil Products Co.), U. S. Patent 2,283,143 (May 12, 1942).

(5) For the discussion of the mechanism of isomerization see the paper by H. S. Bloch, H. Pines and L. Schmerling, THIS JOURNAL, **68**, 153 (1946).

(6) Alfred Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1934.