

twice from hot absolute ethanol (25 cc.): yield, 0.56 g. (62%); m. p. 141–142.5°. Mixed melting point with the benzoate obtained from the low-boiling (ethanolysis) phenol fraction, 141–142.5°.

*Anal.* Calcd. for  $C_{20}H_{21}NO_3$ : C, 59.5; H, 5.26; N, 3.47; alkoxy as methoxyl, 23.1. Found: C, 59.3; H, 5.30; N, 3.60; methoxyl, 22.9.

Repetition of this work starting with 6.3 g. of carefully purified  $\alpha$ -bromo-3,4,5-trimethoxypropiofenone gave identical results and somewhat better yields.

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### Summary

1. Ethanolysis of maple wood with ethanol-hydrochloric acid gives, in addition to the water

insoluble "ethanol lignin," a mixture of distillable oils in amount equal to around 20% of the weight of (Klason) lignin present in the original wood.

2. The mixture contains aldehydic, acidic, phenolic and neutral products. The principal constituents of the phenolic fraction have been identified by analysis and synthesis as  $\alpha$ -ethoxypropioveratrone and  $\alpha$ -ethoxypropiosyringone.

3. These products are in all probability derived from the corresponding hydroxy derivatives either present as such, or formed as fission products from a relatively simple molecular complex.

4. It is suggested that these derivatives ( $\alpha$ -hydroxypropiovanillone and  $\alpha$ -hydroxypropiosyringone), or their dismutation isomers, form the true building-units of which native lignins are composed, or from which "extracted" lignins from hard woods are derived by condensation-polymerization reactions brought about by the extractant.

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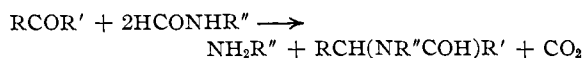
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[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF PHARMACY, UNIVERSITY OF LA PLATA]

## Secondary Amines by the Leuckart Synthesis

BY ARMANDO NOVELLI

The Leuckart synthesis<sup>1</sup> of primary amines by heating ketones with formamide or ammonium formate has been improved by Ingersoll and co-workers.<sup>2</sup> Needing several secondary  $\beta$ -phenylethylamines for pharmacological assays, we varied the Ingersoll adaptation by using the corresponding alkylformamides, and obtained the desired amines, as formyl derivatives, by the general equation



This method has been applied by Wallach<sup>3</sup> to certain alicyclic and terpenoid ketones, but, curiously enough, has been used very little by others. The advantages of simplicity and economy are evident, but possibly have been outweighed, as Ingersoll suggests, by the troublesome procedure, low yields, and formation of secondary and tertiary amines as by-products.

We have found that this method of obtaining secondary amines is general and satisfactory, giving 50–80% yields based on the ketone, taken in

(1) Leuckart, *et al.*, *Ber.*, **18**, 2341 (1885); **19**, 2128 (1886); etc.

(2) Ingersoll, *et al.*, *THIS JOURNAL*, **58**, 1809 (1936).

(3) Wallach, *Ann.*, **343**, 54 (1905).

0.01 to 1 mole lots. Excess of alkylformamide is used (4 moles to 1 of ketone) but the excess is recovered. The secondary amines are obtained directly as hydrochlorides, and are very pure, with no tertiary derivative.

In this paper we describe a number of newly prepared amines and some others previously made only by more complicated procedures. The methyl and ethyl derivatives of phenethylamine were obtained by Busch and Lefhelm<sup>4</sup> from benzalmethylamine and methyl- or ethylmagnesium iodide.

The formyl derivatives were not isolated but were hydrolyzed directly by refluxing with hydrochloric acid. In later papers we hope to discuss the little known mechanism of the Leuckart synthesis and describe a new series of secondary amines from  $\beta$ -phenylethylamines.

### Experimental

**General Method.**—In a distilling flask fitted with a cork bearing a thermometer extending nearly to the bottom is placed 4 moles of alkylammonium formate prepared by adding the proper amine to

(4) Busch and Lefhelm, *J. prakt. Chem.*, [2] **77**, 21, 23 (1908).

TABLE I

Ketones	Amines (as form- amides)	Secondary amine obtained	Yield, %	Hydrochloride	
				M. p., °C.	Cl analyses, % Calcd. Found
Acetophenone	Methyl	<i>dl</i> -Methyl- $\alpha$ -phenethyl <sup>a</sup>	60	178-179	20.69 20.59
<i>p</i> -Methylacetophenone	Methyl	<i>dl</i> -Methyl- $\alpha$ - <i>p</i> -methylphenethyl	50	159-160	19.13 19.17
<i>p</i> -Chloroacetophenone	Methyl	<i>dl</i> -Methyl- $\alpha$ - <i>p</i> -chlorophenethyl	70	199-200	17.39 17.23
<i>p</i> -Bromoacetophenone	Methyl	<i>dl</i> -Methyl- $\alpha$ - <i>p</i> -bromophenethyl	70	196-197	14.20 14.17
Acetophenone	Ethyl	<i>dl</i> -Ethyl- $\alpha$ -phenethyl <sup>b</sup>	70	199-200	19.13 19.17
<i>p</i> -Methylacetophenone	Ethyl	<i>dl</i> -Ethyl- $\alpha$ - <i>p</i> -methylphenethyl	60	217-218	17.77 17.75
<i>p</i> -Chloroacetophenone	Ethyl	<i>dl</i> -Ethyl- $\alpha$ - <i>p</i> -chlorophenethyl	80	<250	16.13 15.97
<i>p</i> -Bromoacetophenone	Ethyl	<i>dl</i> -Ethyl- $\alpha$ - <i>p</i> -bromophenethyl	60	<250	14.20 14.17
Acetophenone	Butyl	<i>dl</i> -Butyl- $\alpha$ -phenethyl	70	154-155	16.62 16.68
<i>p</i> -Methylacetophenone	Butyl	<i>dl</i> -Butyl- $\alpha$ - <i>p</i> -methylphenethyl	50	159-160	15.62 15.62
<i>p</i> -Chloroacetophenone	Butyl	<i>dl</i> -Butyl- $\alpha$ - <i>p</i> -chlorophenethyl	80	174-175	14.31 14.20
<i>p</i> -Bromoacetophenone	Butyl	<i>dl</i> -Butyl- $\alpha$ - <i>p</i> -bromophenethyl	70	174-175	12.42 12.30

<sup>a</sup> Busch and Lefhelm, *loc. cit.*, 173°. <sup>b</sup> *Ibid.*, 201°.

cold formic acid. The temperature is raised slowly to 180-190° and this temperature maintained as long as water distills. After cooling, 1 mole of ketone is added and the mixture heated until boiling begins; water, carbon dioxide, and amine distil and are collected in concentrated hydrochloric acid. In case any ketone distils over, it is returned to the flask at intervals. The temperature of the boiling mixture is 190-230°, which is maintained for four to eight hours, after which the mixture is cooled and diluted with 3-4 volumes of water, giving oily and aqueous layers. The aqueous layer, mixed with the hydrochloric acid used in collecting the distilled amine, is concentrated to give the hydrochloride of the excess of amine used. The oil is refluxed for several hours with 150-200 cc. of hydrochloric acid per mole of ketone taken, and after the hydrolysis is complete water is added, the solution filtered

through moist paper to separate resinified material and the filtrate, if not clear, extracted once or twice with ether. In some experiments the amine hydrochloride crystallizes on cooling. The aqueous solution is made alkaline with ammonia, extracted with ether, the ether solution dried with sodium sulfate and saturated with hydrogen chloride to give the amine hydrochloride. The product is purified further by dissolving in absolute alcohol and precipitating with absolute ether.

Table I summarizes the melting points and analyses of the various hydrochlorides.

### Summary

A new method of obtaining secondary amines, based on the Leuckart synthesis, is described. It has been applied to the preparation of several old and new amines.

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## NOTES

### $\beta$ -Nitrostyrene in the Diene Synthesis

BY C. F. H. ALLEN AND ALAN BELL

In view of a recent paper,<sup>1</sup> we wish to place on record our work on the addition of  $\beta$ -nitrostyrene to dienes. This unsaturated nitro compound added readily to the hydrocarbons listed in Table I, and to the unsaturated ketones, methyleneanthrone and tetraphenylcyclopentadienone; it did not react with furan, sylvan, or 2,5-dimethyl-

furan. In some instances, the products could be distilled *in vacuo* unchanged, whereas in others oxides of nitrogen were evolved even during the addition; thus with methyleneanthrone the principal product was *Bz*-1-phenylbenzanthrone. With the tetracyclone, carbon monoxide was also eliminated and the sole product was the known pentaphenylbenzene.

The addition products are undoubtedly aliphatic nitro compounds (I) since as long as there is an available hydrogen atom in the alpha posi-

(1) Alder, Richert and Windemuth, *Ber.*, **71**, 2451 (1938).