

using alkaline permanganate showed a smooth oxidation to nicotinic acid. As the chief impurity in the earlier preparations of neonicotine was β, γ -dipyridyl, which might also have produced nicotinic acid, little attention was paid to the oxidation.

The methylanabasine fraction was distilled several times, but only the fraction from 270 to 275° was collected. The picrate was formed in fine needles which softened at 215° and melted at 222–223° (corr.) with gas evolution. Some anabasine was methylated by treatment with potassium methyl sulfate, and a picrate was prepared which softened at 217° and melted at 222–223°. When the two were mixed the melting point was 219–220°. Because of the slight differences in the boiling point of the bases and the melting point of their picrates, an optical study was made by Mr. George L. Keenan.

Anabasine Picrate, Natural.—This material consists of yellow, plate-like rods, usually six-sided in outline. In parallel polarized light (crossed nicols), the extinction usually is straight and occasionally inclined. In convergent polarized light (crossed nicols), a biaxial interference figure with the optic axis up or slightly inclined is occasionally seen. The most significant refractive index determinable by the immersion method was the minimum value, n_{α} 1.585, frequently shown on irregular fragments and lengthwise on the elongated forms; n_{β} and n_{γ} were found to be considerably higher than the refractive index for methylene iodide.

Neonicotine Picrate.—The optical crystallographic data for this substance were found to be identical with those obtained for natural anabasine picrate.

Picrate of the Natural Anabasine, Methylated.—This substance crystallizes in small, yellow needles. In parallel polarized light (crossed nicols), the extinction is straight. Biaxial interference figures are rarely seen with convergent polarized light (crossed nicols). The minimum refractive index, n_{α} 1.616, is very common on irregular fragments and on the elongated forms lengthwise; n_{β} and n_{γ} are considerably higher than the refractive index for methylene iodide.

Picrate of the Natural Methyl Anabasine.—This was found to be identical with the previous picrate in so far as optical crystallographic data are concerned.

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Bromomethyl Normal Alkyl Ethers.—Although many investigators have utilized Henry's method¹ for the preparation of α -halogenated ethers to obtain the chloro compounds, the synthesis of the corresponding bromo derivatives has received but scant attention and the preparation and physical properties of only the methyl,^{2,3} ethyl³ and *n*-propyl-³ ethers

¹ L. Henry, *Bull. soc. chim.*, **44**, 458–459 (1885); *Compt. rend.*, **100**, 1007–1009 (1885).

² L. Henry, *Bull. acad. roy. Belgique*, [3] **25**, 439–440 (through *Ber.*, **26**, ref. 933–934 (1893).

³ A. Karvonen, *Ann. Acad. Sci. Fenn.*, (A) **5**, **6**, 109 (through Beilstein, "Handbuch der organischen Chemie," 4th ed., Vol. 1, Supplement 1, p. 305).

have been described in the literature. It is the purpose of this note to record the preparation of the *n*-butyl and *n*-amyl ethers and to correct the erroneous value reported for the index of refraction of the *n*-propyl ether.

Experimental.—A stream of hydrogen bromide gas⁴ was passed into a well-cooled mixture of 75 cc. of aqueous formaldehyde solution and one mole of the appropriate alcohol until saturation occurred with resulting separation of the mixture into two layers. The upper layer was then separated and dried over calcium chloride for at least two hours. Most of the excess hydrogen bromide was removed by placing the ether under a partial vacuum and drawing a small stream of dry air through it, but complete removal of the gas was accomplished only by treating the ether with anhydrous potassium carbonate. Distillation of the crude ether at atmospheric pressure resulted in profound decomposition. However, by maintaining a pressure below 20 mm. it was possible to purify the ethers by fractional distillation. Our experience in purifying these ethers indicates that as the molecular weight increases the stability of these compounds, as indicated by the ease of hydrolysis, markedly decreases. The properties of the ethers synthesized in this investigation are given in Tables I and II.

TABLE I
BROMOMETHYL *n*-ALKYL ETHERS, CH₂Br—O—R

R-	Yield, %	d_4^{20}	n_D^{20}	Molecular refraction		Analyses, Br %		Molecular wts.	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>n</i> -Propyl	80	1.3551	1.4515	29.89	30.32	52.22	52.38	153.0	155.1
<i>n</i> -Butyl	78	1.2702	1.4514	34.48	35.35	47.88	47.87	167.0	171.3
<i>n</i> -Amyl	99	1.2129	1.4512	39.07	40.11	44.14	43.49	181.0	185.5

TABLE II
BOILING POINTS

Bromomethyl <i>n</i> -Propyl Ether									
<i>T</i> , °C. (corr.)....	48	54.6	62.5	71.6	84.0	98.0	133.3		
<i>P</i> , mm.....	20	31	49	73	125	210	747.5		
Bromomethyl <i>n</i> -Butyl Ether									
<i>T</i> , °C. (corr.)	57.2	65.7	73.2	80.8	85.6	90.3	101.0	108.2	159.0
<i>P</i> , mm.....	20	30	45	62.5	76	97	137.5	170	749.5
Bromomethyl <i>n</i> -Amyl Ether									
<i>T</i> , °C. (corr.)	71.8	83	92.2	100.7	113	130.2	140.4	178-180 (dec.)	
<i>P</i> , mm.....	7	15	28	45	76	150	214	748.3	

From Karvonen's³ data for the density and index of refraction for the *n*-propyl ether, the molecular refractivity may be calculated to be 30.73.

⁴ J. H. Kastle and J. H. Bullock, *Am. Chem. J.*, **18**, 105-111 (1896).

A similar calculation using the data in Table I yields 30.32, which is in closer agreement with the calculated value.

CONTRIBUTION FROM THE
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COMMUNICATIONS TO THE EDITOR

THE 4-*n*-ALKYL-GUAIACOLS

Sir:

In a recent paper by Coulthard, Marshall and Pyman [*J. Chem. Soc.*, 280 (1931)] on the variation of phenol coefficients, a number of *n*-alkyl guaiacols were prepared and studied. In view of the fact that the latter compounds were under investigation in the authors' laboratory at a much earlier date [Master of Science Thesis submitted by Norine Hower Howells at the Oklahoma A. and M. College, 1929] and since the methods of synthesis were somewhat different, it appears worth while to report briefly the results of this earlier work.

The 4-*n*-alkyl guaiacols were prepared here by the reduction of the corresponding acyl guaiacols, which were obtained after the method of Howells, Little and Andersen [THIS JOURNAL, 52, 4077 (1930)] by the oxidation of the carbinols resulting through the reaction of the benzoate of vanillin with *n*-alkylmagnesium halides. Unlike the work of Coulthard, Marshall and Pyman, the readily formed solid benzoate ester and diphenyl urethan were selected as derivatives for characterizing the new phenols.

The 4-*n*-pentyl guaiacol (b. p. 156–158° at 20 mm.) which resulted in good yields when 4-*n*-valeryl guaiacol was reduced by the Clemmensen method, was found also to have the maximum phenol coefficient for the series, comparable to the findings of the above authors.

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NORINE HOWER HOWELLS
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INTERMEDIATE PRODUCTS IN THE THERMAL DECOMPOSITION OF AMMONIA

Sir:

An attempt has been made to identify the molecule NH as an intermediate product in the thermal decomposition of ammonia, through a study of the absorption spectrum of the decomposing gas. The emission band at $\lambda\lambda$ 3360–70, long known from photographs of the ammonia–oxygen

⁵ This note is taken from a portion of a thesis submitted by Charles M. Blair in partial fulfilment of the requirements for the degree of Master of Arts.