

salt of the ammono enol modification but no 2-methyl-6-aminopyridine, as in the reaction between solid sodium amide and 2-methylpyridine in boiling xylene.³²

Summary

1. It has been shown that quinolines with an alkyl group in the 2-position may be regarded as cyclic ammono ketone acetals. Particularly is this true because all of the substituted quinolines and pyridines examined react with a liquid ammonia solution of potassium or sodium amide to form highly colored (red or reddish-brown) salts of an ammono enolic modification. Lepidine likewise reacts with the alkali amides to form salts.

2. Salts of the ammono enols of the 2-alkylquinolines, in so far as investigated, react with alkyl halides to form homologous quinolines with a lengthened side chain. It was shown that the potassium salts of the ammono enols of 2-ethyl- and 2-*n*-propylquinolines react with ethyl bromide and methyl iodide, respectively, to form the same product, 2-*sec*-

butylquinoline. The group, $\begin{matrix} \text{RCH}_2 \\ \diagup \\ \text{C}=\text{N}- \\ \diagdown \\ \text{R} \end{matrix}$, is therefore converted by potassium amide to the group, $\begin{matrix} \text{RCH} \\ \diagup \\ \text{C}=\text{NK}- \\ \diagdown \\ \text{R} \end{matrix}$, as would be expected from

the known mode of enolization of the ketones of the water system. 4-Methylquinoline (lepidine) was converted, through its potassium salt, into 4-ethyl- and 4-*n*-propylquinoline.

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THE ALPHA-CHLOROETHYL NORMAL ALKYL ETHERS¹

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Although the preparation of the α -chloromethyl normal alkyl ethers has been reported by a large number of investigators, the series being complete through the amyl derivative,² the syntheses of only three of the α -chloroethyl normal alkyl ethers have been recorded, namely, the methyl,³ ethyl,⁴

³² Seide, *J. Russ. Phys.-Chem. Soc.*, **50**, 534 (1920).

¹ An abstract of the dissertation submitted by J. T. Murchison to the Faculty of the University of Texas, in partial fulfillment of the requirements for the degree of Master of Arts, August, 1930.

² J. Bliss Norton, "Dissertation," University of Texas, 1930.

³ (a) Rübenkamp and Geuther, *Ann.*, **225**, 269-270 (1884); (b) Favre, *Bull. soc. chim.*, [3] **11**, 1096 (1894); (c) Gauthier, *Ann. chim.*, [8] **16**, 311-313 (1909); (d) Madinaveitin and Puyal, *Anales soc. españ. fis. quim.*, **16**, 329-337 (1918), (through *C. A.*, **13**, 2677 (1919)).

⁴ (a) Wurtz and Frapolli, *Ann.*, **108**, 226-227 (1858); (b) Geuther and Bachmann, *ibid.*, **218**, 39 (1883); (c) Jacobson, *Ber.*, **4**, 215 (1871); (d) Fritsch and Schumacher, *Ann.*, **279**, 302-303 (1894); (e) Geuther and Laatsch, *ibid.*, **218**, 21 (1883);

and *n*-propyl^{8c} ethers. These have been insufficiently characterized; only the first member of this series, the α -chloroethyl methyl ether, has had physical properties recorded other than the boiling point and this at unspecified pressure. The paucity of such information, as well as the lack of agreement concerning the data recorded, is clearly indicated in Table I.

TABLE I
Boiling point,
°C.

	Boiling point, °C.	Density	Index of refraction
Rübencamp and Geuther	72-75	0.996 ¹⁷
Favre	80	1.023 ¹⁸	1.401 ¹⁹
Gauthier	No data		
Madinaveitin and Puyal	No data		

For the ethyl ether the variation in the boiling points reported is equally marked, as may be seen in Table II.

TABLE II

Boiling point, °C.	Wurtz and Frapolli	Geuther and Bachmann	Jacobson	Fritsch and Schumacher	Swallen and Boord
	98	97-98	97-98	85-90	93-96

In view of the lack of information concerning the properties of the ethers of this series, together with the disagreement in the physical data now reported in the literature, it has been our purpose: (1) to prepare the first three members of the normal series to establish the properties in dispute and to obtain further data concerning them; (2) to extend this series through the amyl ether.

In the preparation of the α -chloroethyl ethers Gauthier's^{8c} modification of the method of Wurtz and Frapolli^{4a} was used. This consisted in saturating with dry hydrogen chloride gas a well-cooled mixture of equimolecular quantities of paraldehyde and the alcohol whose α -chloroethyl derivative was desired. The crude chloro ether was separated and dried over anhydrous calcium chloride for not more than two hours, longer drying resulting in marked decomposition. Due to the rapid evolution of hydrogen chloride during drying, it was advisable to maintain the ethers at a low temperature. The chloro ethers were freed from residual hydrogen chloride by drawing through them a current of dry air under a partial vacuum for a period of about two hours.

The constants obtained for the methyl ether are recorded in Table III. The boiling point and density obtained agree most nearly with those reported by Rübencamp and Geuther,^{3a} but the index of refraction corresponds to that recorded by Favre.^{3b}

As seen in Table III, the temperature observed for the boiling point of the ethyl ether is in agreement with that of the first three investigators. Gauthier, Ref. 3c; Madinaveitin and Puyal, Ref. 3d; (f) Swallen and Boord, THIS JOURNAL, 52, 654 (1930).

The boiling point of the propyl ether as determined by Gauthier,³ is in approximate agreement with our result. The properties of the five ethers synthesized in this investigation are collected in Table III.

TABLE III
 α -CHLOROETHYL *n*-ALKYL ETHERS, $\text{CH}_3\text{CHCl}-\text{O}-\text{R}$

R	B. p., ^a °C.	Mm.	Yield, %	d_4^{20}	n_D^{20}
Methyl	72-73	751	97	0.9902	1.4004
Ethyl	97.5	750	94	.9537	1.3950
<i>n</i> -Propyl ^b	47.5	40	93	.9322	1.4013
<i>n</i> -Butyl	48.9-50.3	11	95	.9335	1.4155
<i>n</i> -Amyl	63.3-66.3	8	99	.9200	1.4218

R	Molecular refractivity		Analyses, Cl, %		Molecular wts.	
	Calcd.	Obs.	Calcd.	Found	Calcd.	Found
Methyl	22.43	23.17	37.51	38.76	94.52
Ethyl	27.14	27.29	32.68	32.55	108.53	108.00
<i>n</i> -Propyl	32.09	31.74	28.93	24.51	122.57	121.63
<i>n</i> -Butyl	36.47	36.67	26.22	26.19	136.56	131.79
<i>n</i> -Amyl	40.95	41.57	23.54	23.42	150.56	151.20

^a All temperatures reported are corrected. ^b After this investigation was completed, Dykstra, Lewis and Boord, THIS JOURNAL, 52, 3399-3400 (1930), reported the preparation of both the *n*-propyl and the *n*-butyl ethers. However, no physical data concerning these compounds were reported.

The α -chloroethyl ethers were found to be extremely reactive. In the presence of moisture they hydrolyze with great rapidity, yielding the original materials, and upon standing dry they polymerize, forming dark tarry residues. Particularly noticeable is the fact that the higher members of the series are less stable than those of less carbon content.

Grateful acknowledgment is made to Mr. Francis C. Usher for his aid in the preparation of the ethyl and *n*-propyl ethers.

Summary

1. The methyl, ethyl and *n*-propyl α -chloroethyl ethers have been resynthesized and certain constants determined.

2. This series has been extended by the preparation of the *n*-butyl and the *n*-amyl ethers. Certain properties of these new ethers have been determined.

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