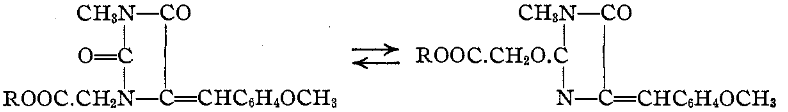
defined pairs of geometrical isomers. Isomerism of this type is particularly interesting among hydantoin derivatives. Incidentally the observation has been made that ethyl N-1-methyl-anisal-hydantoin-3-acetate seems to split off an acetic acid residue during the course of some of its transformations. This fact deserves attention since a hydrocarbon residue in union with nitrogen is commonly assumed to be present in a compound in a very stable form of combination. If, however, the assumption is admissible that the ester, m. p. 107–108°, is tautomeric in the sense



I II

and that alkali favors the enolic modification, the splitting off of the acetate group could readily be understood because of the fact that compounds of this type have been studied and have been found to be unstable.

The intense hydrolysis of the polypeptide-hydantoin has resulted in its decomposition with the formation of the mixed aliphatic-aromatic imidodibasic acid

$$\underset{\displaystyle COOH}{\underset{|}{CH_2}}NH.\underset{\displaystyle COOH}{\underset{|}{CH}}\ CH_2C_6H_4OH$$

The barium salts and ethyl ester are described in this paper, but a detailed description of the free acid and its other derivatives is being reserved for a later publication.

SOUTH HADLEY, MASSACHUSETTS

[CONTRIBUTION FROM MELLON INSTITUTE OF INDUSTRIAL RESEARCH AND THE COLLEGE OF PHARMACY, UNIVERSITY OF PITTSBURGH]

SYNTHESES WITH β,β'-DICHLORO-DIETHYL ETHER

BY LEONARD H. CRETCHER[1] AND W. H. PITTENGER[2]

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Introduction

β,β'-Dichloro-diethyl ether is a by-product formed during the manufacture of ethylene chlorohydrin and, as such, is available in comparatively large amounts. So far, no use has been made of this substance and its reactions have been little studied. It was first described by Kamm and Waldo,[3] who established its constitution on the basis of the fact that, on boiling with aniline and 10% aqueous sodium hydroxide, it formed 4-phenyl-morpholine.

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[3] Kamm and Waldo, THIS JOURNAL, **43,** 2223 (1921).

The authors are making a detailed study of this ether with the end in view of preparing possible useful derivatives and comparing its properties with those of its well known sulfur analog, "mustard gas." This preliminary paper is limited to a statement of the results obtained by reaction of sodium alcoholates, aromatic primary amines, and the sodium salts of organic acids on the ether in question. In every case, the expected products were obtained, ethers $ROCH_2CH_2OCH_2CH_2Cl$ or $(ROCH_2CH_2)_2O$ by the action of alcoholates, morpholines $RN(CH_2CH_2)_2O$ by the action of aromatic primary amines, and esters $ROCOCH_2CH_2OCH_2CH_2Cl$ or $(ROCOCH_2CH_2)_2O$ by the action of the sodium salts of organic acids.

Experimental Part

Action of Sodium Alcoholates.—Sodium alcoholates have no apparent action on this ether at room temperature. The reaction, once started on a water-bath, proceeds quite rapidly for a short time, after which, in general, from 8 to 15 hours' heating is necessary to cause the formation of the calculated amount of sodium chloride. The by-products of the reactions are of lower boiling point than the main fraction and have not been identified as yet.

To prepare the β-chloro-β′-methoxy ether described below, equimolecular proportions of sodium methylate in methyl alcohol, and dichloroether were heated together on a water-bath until neutral. The dialkyl ethers were prepared in the same manner, the necessary alcoholate being used in 10% excess of the calculated amount. After the reaction was finished, the sodium chloride was removed by filtration and the product purified by distillation.

The chloro-methoxy ether is soluble in alcohol and ether and slightly so in water. The dialkyl ethers are soluble in alcohol and ether. They decrease in solubility in water as the molecular weight increases, the dimethyl compound being very soluble and dibutyl only to a slight extent. The dialkyl ethers are much more soluble in cold than in hot water.

TABLE I

ALKYL ETHERS PREPARED

						Analysis					
						Calcd.			Found		
Diethyl ether	Formula	Boiling point °C. corr.	Mm.	d_{15}^{15}	Yield %	C %	H %	Cl %	C %	H %	Cl %
β-chloro-β′-methoxy	$C_6H_{11}O_2Cl$	169	744	1.0562	58	43.32	7.94	25.63	42.95	8.17	25.76
bis(β-methoxy)	$C_6H_{14}O_3$	161.5	736	0.9514	36	53.73	10.44	...	53.65	10.71	...
bis(β-ethoxy)[a]	$C_8H_{18}O_3$	187	735	.9149	41	59.26	11.11	...	58.99	11.06	...
bis(β-propoxy)	$C_{10}H_{22}O_3$	219	737	.8877	40	63.16	11.58	...	62.90	11.63	...
bis(β-butoxy)	$C_{12}H_{26}O_3$	250–252	741	.8847	45	66.05	11.92	...	66.01	12.17	...

[a] Approximately the same percentage yield was obtained when 71 g. of dichloroether and 90 g. of potassium hydroxide, in solution in 175 cc. of 95% ethyl alcohol, were heated overnight on a water-bath.

Action of Aromatic Primary Amines.—When a mixture of equimolecular proportions of dichloro-ether and amine was boiled with a large excess of 35% aqueous sodium hydroxide for about 15 hours, reaction took place with the formation of a morpholine derivative in a yield of about 35%. Water was then added and the containing flask placed in an ice-bath overnight, during which time the viscous product of the reaction solidified almost completely. After filtering off the solid and removing by suction as much of the oil as possible, the solid material was placed in a Claisen flask and distilled under reduced pressure. On standing for some hours, the distillate, in all cases, solidified and was recrystallized from dil. ethyl alcohol to constant melting point. The amines used were *p*-toluidine, α-naphthylamine and β-naphthylamine.

TABLE II

MORPHOLINES PREPARED

					Analysis	
					Calcd.	Found
Morpholine	Formula	B. p. °C. corr.	Mm.	M. p. °C.	N %	N %
4-*p*-tolyl	$C_{11}H_{15}ON$	167	30	51	7.92	7.88
4-β-naphthyl	$C_{14}H_{15}ON$	239	30	90	6.57	6.46
4-α-naphthyl[a]	$C_{14}H_{15}ON$	...	..	83	6.57	6.51

[a] Owing to its tendency to sublime and the difficulties encountered in attempting to distil it, this compound was sublimed in a vacuum from the crude reaction product and purified by crystallization from dil. alcohol.

Action of Sodium Salts of Organic Acids.—Esters could not be successfully prepared by heating the dichloro-diethyl ether and the sodium salts alone. Reaction did take place, however, when a small amount of diethylamine was added to the mixture. The use of amines as catalysts for such reactions was suggested in the patent literature.[4]

For the preparation of the esters herein described, equimolecular proportions of dichloro-diethyl ether and the dry sodium salt of the necessary acid were mixed, a few drops of diethylamine added, and the mixture was heated in an oil-bath and constantly stirred. To prepare *bis*(β-acetoxy-ethyl) ether the bath was kept at a temperature of 190° and the reaction continued for seven hours. In preparing β-chloro-β′-benzoxy-diethyl ether and *bis*(β-benzoxy-ethyl) ether, the conditions were 140° for three hours and 200° for five hours, respectively. After the mixture had cooled,

TABLE III

ESTERS PREPARED

						Analysis					
						Calcd.			Found		
Diethyl ether	Formula	Boiling point °C. corr.	Mm.	d_{15}^{15}	Yield %	C %	H %	Cl %	C %	H %	Cl %
bis(β-acetoxy)[a]	$C_8H_{14}O_5$	148	26	1.1078	45	50.52	7.37	...	50.25	7.60	...
β-chloro-β′-benzoxy[b]	$C_{11}H_{13}O_3Cl$	191	25	1.1841	44	...	..	15.53	...	..	15.21
bis(β-benzoxy)	$C_{18}H_{18}O_5$	279–281	24	1.1701	55	68.79	5.73	...	68.36	5.93	...

[a] Previously prepared by Wurtz [*Ann. chim.*, [3] **69**, 355 (1863)].

[b] Thirteen per cent. of dibenzoate was also obtained from this reaction.

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[4] Ger. pat. 268,621, **1913**; U. S. pat. 1,260,289, **1918**.

water was added and the ester extracted with ether. The ether solution was dried over sodium sulfate and the product distilled.

Bis-(β-acetoxy-ethyl)ether was hydrolyzed to the corresponding dihydroxy compound by heating with a methyl alcoholic solution of hydrogen chloride.[5] The yield of dihydroxy ether was 51%. This compound was previously made by Lourenco.[6]

Summary

Several new compounds have been prepared from β,β'-dichloro-diethyl ether by reaction with sodium alcoholates, aromatic primary amines and sodium salts of organic acids.

The study of this ether will be continued.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

IDENTIFICATION OF AMINES. II. META-NITROBENZENE-SULFONAMIDES

BY C. S. MARVEL, F. L. KINGSBURY AND F. E. SMITH

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The general use of benzenesulfonyl chloride for the separation and identification of primary and secondary amines has suggested the use of substituted benzenesulfonyl chlorides in order to obtain more easily crystallizable compounds. The *p*-bromobenzene-sulfonamides[1] were found to be of considerable use for identification purposes, although they could not be used for the separation of primary and secondary amines on account of the alkali insolubility of the primary amine derivatives.

The *m*-nitrobenzene-sulfonamides have now been studied. They are all easily prepared and purified and are therefore suitable for use in identification. In addition almost all of the common primary amines give derivatives that are soluble in alkalies, so that separations of primary and secondary amines may be made through the amides. The only primary amine derivative that has been found to be but slightly soluble in alkalies is that of *p*-bromo-aniline.

The nitrobenzenesulfonyl derivatives of diethylamine, di-*n*-butylamine and the mono-alkyl anilines are particularly useful as derivatives for identification, since the common reagents give oils or low-melting solids that crystallize only with considerable difficulty.

Experimental Part

Two procedures were used to prepare the sulfonamides. They worked equally well. *m*-Nitrobenzenesulfonyl chloride was treated with a slight

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[5] Gattermann's "Methods of Organic Chemistry;" Schober and Babasinian's translation, MacMillan Co., third ed., **1914**, p. 198.

[6] Lourenco, *Ann. chim.*, [3] **67**, 257 (1863).

[1] Marvel and Smith, THIS JOURNAL, **45**, 2696 (1923).