dery crystals, later found to be chiefly the *dl*B*dl*A salt. The first two crops after two recrystallizations obtained by slowly cooling the liquid gave 10.7 g. of completely pure *l*B*d*A salt; m. p., 184° (corr.).

Rotation. Subs., 2.0017 g. and ammonium molybdate 0.2000 g., made up to 50 cc. in water at 20°: $\alpha_D = +1.50°$ in a 2-dm. tube; $[\alpha]_D^{20} = +18.5°$.

***l*-Phenylethylamine.**—The base was obtained from the *l*B*d*A salt in the usual way but was not distilled. The rotation was observed in aqueous solution.

Rotation. Subs., 1.5505 g. made up to 50 cc. in water and a few drops of alcohol: $\alpha_D = -1.43°$ in a 2-dm. tube: $[\alpha]_D = -23.1°$. Kipping and Hunter[13] found $[\alpha]_D = -25°$.

***dl*-Phenylethylamine-*dl*-malate.**—From the mother liquors of the *l*B*d*A salt, the *dl*B*dl*A salt was obtained. After two recrystallizations it still gave a slight dextrorotation. On slow cooling it formed coarse prisms; m. p., 161–161.5° (corr.). The salt prepared from the *dl*-base and *dl*-acid was similar in appearance and melted at 162° (corr.). The sirupy mother liquor was not further examined.

The solutions remaining from the hydrolysis of the *d*B*l*A and *l*B*d*A salts with sodium hydroxide were evaporated to dryness on the water-bath for the recovery of the active sodium malates. The isolation of the free acids was not attempted.

Summary

1. A new general method for obtaining both pure active forms of an optically inactive base is described. Only one active form and the inactive form of the acid used for the resolution are required. The other active form of the acid is also obtained in the process.

2. The method has been used for the complete resolution of phenylamino-acetic acid and camphor-sulfonic acid, and α-phenylethylamine and malic acid, respectively. Several new salts are described.

NASHVILLE, TENNESSEE

[CONTRIBUTION FROM THE FELLOWSHIP OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, AND SCHOOL OF PHARMACY, UNIVERSITY OF PITTSBURGH]

FURTHER SYNTHESES WITH β,β'-DICHLORO-DIETHYL ETHER

BY LEONARD H. CRETCHER, JULIUS A. KOCH AND W. H. PITTENGER

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In a recent paper from this Laboratory[1] it was shown that the chlorine in β,β'-dichloro-diethyl ether can be removed by reaction with sodium alcoholates, aromatic primary amines and the sodium salts of organic acids, with the formation of the expected ethers, substituted morpholines and esters. This work has been continued to include a study of the action of the sodium salts of phenol, thiophenol and naphthols, potassium phthalimide and sodium hydroxide. Further experiments leading to an improvement in the previously described method for preparing substituted morpholines have also been made.

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[13] Kipping and Hunter, *J. Chem. Soc.*, **83**, 1147 (1903).

[1] Cretcher and Pittenger, THIS JOURNAL, **47**, 163 (1925).

Experimental Part

Action of Aromatic Primary Amines.—It was previously reported that the yield of substituted morpholine obtained by boiling β,β'-dichloro-diethyl ether with aromatic primary amines and aqueous sodium hydroxide was about 35% of the calculated amount.[2] It has since been found that a much better yield can be obtained by heating one molecular proportion of the chloro-ether with three molecular proportions of amine for some time at 200–215°. The details of one experiment will illustrate the general procedure.

Twelve g. of β,β'-dichloro-diethyl ether was heated in an oil-bath to 200° with 27 g. of *p*-toluidine, for two hours. After cooling, benzene was added to extract the morpholine, and the insoluble amine hydrochloride was separated by filtration. The benzene was removed by distillation, and the residue distilled and recrystallized thrice from dil. alcohol. The weight of 4-*p*-tolyl-morpholine was 11.5 g., or 77% of the calculated amount.

4-Phenyl-morpholine, 4-β-naphthyl-morpholine, and 4-α-naphthyl-morpholine were prepared according to the method described above from dichloro-ether and aniline, β-naphthylamine and α-naphthylamine, in yields of 65%, 72% and 68%, respectively.

Bis(β-anilino-ethyl)ether, $(C_6H_5NHCH_2CH_2)_2O$.—On distillation of the crude 4-phenyl-morpholine, a small amount of high-boiling material was obtained which solidified on cooling. It crystallized from alcohol in lustrous plates; m. p., 115.5°.

Anal. Calcd. for $C_{16}H_{20}ON_2$: N, 10.93. Found: 10.85.

Action of the Sodium Salts of Phenol, Thiophenol and Naphthols.—For the preparation of the chloro-ethers mentioned in this series one molecular proportion of sodium was dissolved in absolute ethyl alcohol, then the calculated amount of phenol or thiophenol was added and the

TABLE I

AROMATIC ETHERS PREPARED

	Diethyl ether	Formula	Boiling point °C.	Mm.	d_{15}^{15}	Yield %
1	βChloro-β'-phenoxy-	$C_{11}H_{13}O_2Cl$	149	10	1.149	60
2	Bis(β-phenoxy)-	$C_{16}H_{18}O$	m. p. 66	..	...	82
3	βChloro β'-phenylmercapto-	$C_{10}H_{18}OClS$	158	4	1.1799	60
4	Bis(β-phenylmercapto)-	$C_{16}H_{18}OS_2$	257–258	16	1.1561	79
5	Bis(β-naphthoxy)-	$C_{24}H_{22}O_3$	m. p. 122	..	....	56
6	Bis(α-naphthoxy)-	$C_{24}H_{22}O_3$	m. p. 87	..	....	52

	Analyses					
	Calcd.			Found		
	C %	H %	Cl %	C %	H %	Cl %
1	..	..	17.7	...	..	17.88
2	74.41	6.98	...	74.23	7.27	...
3	...	..	16.39	...	..	16.40
4	66.2	6.22	...	66.19	6.5	...
5	80.44	6.14	...	80.49	6.27	...
6	80.44	6.14	...	80.26	6.07	...

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[2] Ref. 1, p. 165.

mixture heated with dichloro-ether on a water-bath overnight. The salt was filtered off, washed with a little alcohol, and the filtrate distilled.

For the preparation of the disubstituted ethers, a 5% excess of the sodium salt of the phenolic compound was used. The procedure was otherwise the same as described above.

Action of Potassium Phthalimide.—In the preparation of the phthalimido derivatives of diethyl ether from dichloro-ether and potassium phthalimide, it was found necessary to add a few drops of diethylamine to catalyze the reaction. Molecular proportions of the halogen ether and potassium phthalimide were intimately mixed, the catalyst was added, and the mixture stirred and heated in an oil-bath. To prepare the monochloro-monophthalimido derivative, the heating was continued for three hours at 125°; for the diphthalimido compound, four hours at 135–140° was required.

TABLE II

PHTHALIMIDO ETHERS PREPARED

Diethyl ether	Formula	M. p. °C.	Yield %	Analyses Calcd. N %	Analyses Found N %
βChloro-β'-phthalimido-[a]	$C_{12}H_{12}O_3NCl$	69	95	5.52	5.42
Bis(β-phthalimido)-[b]	$C_{20}H_{16}O_5N_2$	159	55	7.69	7.66

[a] β-Amino-β'-chloro-diethyl ether was not isolated from the material resulting from hydrolysis of this compound with concd. HCl. The solid material obtained was largely ammonium chloride.

[b] Previously prepared by Gabriel[3] and described as sintering at about 152° and melting at 156.5°. Gabriel hydrolyzed the compound with formation of bis(β'-amino-ethyl) ether.

Action of Sodium Hydroxide.—β,β'-Dichloro-diethyl ether is resistant in a marked degree to the action of hot aqueous sodium hydroxide. In an attempt to prepare divinyl ether, 429 g. of dichloro-ether was mixed in an iron pot with 450 g. of flake sodium hydroxide.

A 95cm. Crismer distilling column was connected to the pot, which was then immersed in an oil-bath and heated. Distillation began when the oil was at 200°. The temperature was maintained at 200–220° for about six hours, after which distillation ceased. A free flame was then applied and a few cubic centimeters more of distillate was obtained. Throughout the course of the heating, the temperature of the vapor remained constant at 84–85°. The distillate consisting of water and an immiscible organic layer weighed 269 g. The odor of acetaldehyde being noticed, the product was transferred to a flask, without separating the layers, and distilled through a long column. Twenty g. of acetaldehyde was obtained at 21° and about half as much divinyl ether at 39°. The temperature then rose to 84° and the distillation was discontinued. As much solid potassium hydroxide as would dissolve was then added to the undistilled fraction, the layers were separated, and the non-aqueous layer was dried over potassium hydroxide and distilled; 180 g. of product was obtained, boiling at 107° (734 mm.). This material contained chlorine and was unsaturated; furthermore, when it was mixed with water and treated with dil. acid, the odor of acetaldehyde became at once evident

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[3] Gabriel, *Ber.*, **38**, 3413 (1905).

and the layers became miscible. These properties, together with the fact that the boiling point was exactly midway between the boiling points of divinyl ether and dichloro ether, suggested that we were dealing with β-chloro-ethyl-vinyl ether. The results of chlorine analyses were as follows.

Calcd. for C_4H_7OCl: Cl, 33.3. Found: 25.9, 26.0.

It was therefore considered that the liquid was a constant-boiling mixture of approximately 78% of chloro-ethyl-vinyl ether and 22% of some chlorine-free substance.

In order to prove the presence of the chloro-ethyl-vinyl ether, 100 g. of the liquid was boiled in absolute alcoholic solution until neutral, with an amount of sodium diethylmalonate equivalent to the chlorine actually found by analysis. After the salt formed had been filtered out and the alcohol removed, the filtrate was distilled under reduced pressure. The main fraction boiled at 130–135° (9 mm.). On redistillation, it boiled at 122° corr. (3 mm.). The yield of diethyl vinyl-oxyethyl malonate[4] was 73% of the calculated amount; d_{15}^{15}, 1.0575.

Anal. Calcd. for $C_{11}H_{18}O_5$: C, 57.39; H, 7.82. Found: C, 57.51; H, 7.93.

The presence of β-chloro-ethyl-vinyl ether having been demonstrated, it remained to separate the mixture. Diethylene dioxide (1,4-dioxane) was thought to be a chlorine-free substance that might well be formed under the conditions of this experiment. Inasmuch as the dioxane is known to be soluble in water, a sample of the mixture boiling at 107° was extracted eight times with small amounts of water, after which the water-insoluble layer was dried over solid potassium hydroxide and distilled. The whole of the material boiled between 108° and 111°. On redistillation, the boiling point was 109° corr. (740 mm.); d_{15}^{15}, 1.0525.

Anal. Calcd. for C_4H_7OCl: Cl, 33.33. Found: 33.30.

β-Chloro-ethyl-vinyl ether is very stable in the presence of alkali, but readily undergoes hydrolysis in the presence of dilute acid in the cold, and more rapidly when heated, forming acetaldehyde and ethylene chlorohydrin quantitatively, doubtless according to the following equations: $ClCH_2CH_2OCH{=}CH_2 + HOH = ClCH_2CH_2OH + CH_2{=}CHOH$; $CH_2{=}CHOH = CH_3.CHO$. Twenty g. of β-chloro-ethyl-vinyl ether was added to 30 cc. of water, 5 drops of concd. hydrochloric acid were added, and the mixture was distilled. At 21° the calculated amount—8.3 g.—of acetaldehyde was obtained, the temperature then rising to 96°, where 35 cc. of distillate was obtained. The boiling point and specific gravity of this liquid correspond to those of the constant boiling, 40% ethylene chlorohydrin solution. Furthermore, on treatment with sodium hydroxide, ethylene oxide was evolved.

The water solution remaining after making the extractions was saturated with potassium hydroxide, whereupon the liquid separated into two layers. The upper layer was dried over solid potassium hydroxide and distilled over sodium. The boiling point was 100.5° corr. (740 mm.). The compound formed a solid addition product with sulfuric acid and with bromine. When put in a test-tube and cooled to 5° it solidified, to melt again at 9°. These properties identify the compound as 1,4-dioxane, $O(CH_2CH_2)_2O$.

The above results show that the action of dry sodium hydroxide on β,β'-dichloro-diethyl ether at temperatures around 200° produces mainly a constant-boiling mixture of β-chloro-ethyl-vinyl ether, 1,4-dioxane, and water, together with small amounts of acetaldehyde and divinyl ether.

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[4] This ester and its derivatives condense with urea, forming vinyl-oxyethyl- and substituted vinyl-oxyethyl-barbituric acid derivatives which on treatment with dilute mineral acid form hydroxylethyl-barbituric acids. A paper on this subject is now in course of preparation.—L. H. C.

Summary

The behavior of β,β'-dichloro-diethyl ether, under definite conditions, with aromatic primary amines, the sodium salts of phenol, thiophenol and naphthols, potassium phthalimide and dry sodium hydroxide has been studied and several of the resulting compounds have been described.

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[Contribution from the Bureau of Chemistry, United States Department of Agriculture]

THE NON-VOLATILE ACIDS OF THE STRAWBERRY, THE PINEAPPLE, THE RASPBERRY AND THE CONCORD GRAPE

By E. K. Nelson

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Kunz and Adam[1] state that strawberries and raspberries contain citric acid but no malic acid. Krzizan and Plahl[2] and Krzizan[3] found only citric acid in raspberries. Kayser[4] reports citric acid as the principal acid of raspberries, but found malic and tartaric acids also. Jorgensen[5] found that citric acid predominates in raspberries, with a little malic acid and traces of succinic acid but no tartaric acid. Muttelet[6] states that strawberries and raspberries contain citric acid, with traces of tartaric acid but no malic acid. Paris[7] reports the presence of citric acid and a little malic acid in strawberries. Kayser[8] states that the pineapple contains citric acid but no malic or tartaric acid. Bigelow and Dunbar[9] found in the red raspberry probably citric acid alone (malic acid, if present, in traces only). C. Garino-Canina[10] calls attention to the presence of malic acid in the grape and concludes that the relative proportion depends on geographical area and meteorological conditions.

In view of the conflicting nature of these statements in the literature regarding the non-volatile acids of fruits, an investigation was undertaken to determine, by the ester-distillation method, the character of the nonvolatile acids in strawberries, pineapples, raspberries and grapes.

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[1] (a) Kunz and Adam, *Z. Osterr. Apoth. Ver.*, **44**, 187 (1906). (b) *Z. Nahr. Genussm.* **12**, 670 (1906).

[2] Krzizan and Plahl, *ibid.*, **11**, 205 (1906).

[3] Krzizan, *Z. Offentl. Chem.*, **12**, 323, 342 (1906).

[4] Kayser, *ibid.*, **12**, 155, 191 (1906).

[5] Jorgensen, *Z. Nahr. Genussm.*, **13**, 241 (1907).

[6] Muttelet, *Ann. fals.*, **2**, 383 (1909).

[7] Paris, *Chem.-Ztg.*, **26**, 248 (1902).

[8] Kayser, *Z. Offentl. Chem.*, **15**, 187 (1909).

[9] Bigelow and Dunbar, *J. Ind. Eng. Chem.*, **9**, 762 (1917).

[10] Garino-Canina, *Ann. chim. applicata*, **5**, 65 (1916).