TABLE II

17-KETOSTEROIDS FROM THE OZONIZATION OF 20-ENOL ACETATES

No.	Derivatives of 17-ketoetiocholane	Obt. from	Cryst. form	Solvent	M. p.[e] °C.	$[\alpha]_D$[g]	Formula	Composition, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
7	3(α)-Hydroxy[a]	1	Needles	C_6H_6-lig.	151 –152[f]	+109	$C_{19}H_{30}O_2$		[i]		
8	3(α),11(α)-Diacetoxy	2	Needles	Ligroin	170.5–172	+ 43	$C_{23}H_{34}O_5$	70.74	70.47	8.78	8.80
9	3(α)-Hydroxy-11(α)-acetoxy	8	Prisms	Ligroin	147 –148	+ 25	$C_{21}H_{32}O_4$	72.38	72.17	9.26	9.63
10	3(α),11(α)-Dihydroxy	8, 9	Prisms	Et acet.	170.5–171	+ 80	$C_{19}H_{30}O_3$	74.47	74.43	9.87	9.55
11	3(α),12(α)-Diacetoxy[b]	3	Prisms	Acetone–lig.	156 –157	+193[h]	$C_{23}H_{34}O_5$	70.74	70.71	8.78	8.75
12	3(α),12(α)-Dihydroxy[c]	11	Needles	Et acet.	164.5–165	+167	$C_{19}H_{30}O_3$	74.47	74.50	9.87	9 54
13	3(β)-Hydroxy-allo[d]	5, 6	Prisms	Et acet.-lig.	174 –175	+ 97	$C_{19}H_{30}O_2$		[i]		

[a] Reported values,[5] m. p. 150–151°;[6] m. p. 151–152°, transition point, 140–142°; $[\alpha]_D$ +100°; $[\alpha]_{5461}$ +130° (ethanol). [b] Reported values,[7] m. p. 162–162.5°; $[\alpha]_D$ +176°; $[\alpha]_{5461}$ +214° (acetone);[8] m. p. 157–158.5°; $[\alpha]_D$ +179° (acetone). [c] Reported values,[4] m. p. 165.5–168°; m. p. 164–165°.[8] No rotation reported. [d] Reported values,[9] m. p. 174–174.5°; $[\alpha]_D$ +87° (methanol). [e] All melting points are corrected. [f] Softens at 140°. [g] In $CHCl_3$. [h] +177° in acetone. [i] Identified by melting point of a mixture and comparison of the infrared spectrum with an authentic specimen. The infrared spectra were determined and compared by Dr. Konrad Dobriner, Sloan–Kettering Institute, New York 21, N. Y., to whom we extend our thanks.

Enol Acetate of *3(α),12(α)-Diacetoxy-20-keto-21-benzalpregnane*.—This substance is obtained as one of the reaction products from the acetylation of the dihydroxy benzal derivative by heating twenty-four hours with acetic anhydride and pyridine. It is also obtained in small amounts from the acetylation catalyzed with perchloric acid according to the method of Whitman and Schwenk,[10] especially if the reaction mixture is permitted to stand at room temperature for forty-five minutes. It is most readily separated by chromatography upon aluminum oxide or by fractional crystallization of the acetylation product from acetone. It was recrystallized from glacial acetic acid, and its characteristics are recorded in Table I.

3(α)-Acetoxy-12(α)-hydroxy-20-keto-21-benzalpregnane.—When 3(α),12(α)-dihydroxy-20-keto-21-benzalpregnane is acetylated using milder conditions (pyridine-acetic anhydride at room temperature; acetic anhydride in the presence of low concentrations of perchloric acid at 5° for ten minutes), the 3-monoacetoxy derivative is obtained in good yield. The product was recrystallized from acetone as plates, m. p. 210–211°; $[\alpha]^{21}_D$ +177° (ethanol).

Anal. Calcd. for $C_{30}H_{40}O_4$: C, 77.25; H, 8.69. Found: C, 77.57; H, 8.68.

Upon more vigorous acetylation with either pyridine and acetic anhydride or with acetic anhydride and sodium acetate, the monoacetate is converted to the known diacetate,[3] m. p. 123–126°.

Summary

1. The conversion of 20-ketosteroids to 17-ketosteroids was accomplished by preparation of the enol acetates followed by ozonolysis.

2. 3(α)-Hydroxy-17-ketoetiocholane, 3(β)-hydroxy-17-ketoetioallocholane, 3(α),12(α)-dihydroxy-17-ketoetiocholane, and 3(α),11(α)-dihydroxy-17-ketoetiocholane were prepared in this way.

3. The enol acetate of 3(β)-hydroxy-20-keto-allopregnane was obtained in two forms which were shown to be geometric isomers by ozonolysis to isoandrosterone.

4. The enol acetate of 3(α),12(α)-diacetoxy-20-keto-21-benzalpregnane was prepared and its ultraviolet absorption spectrum is described.

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[5] Ruzicka, Goldberg, Meyer, Brüngger and Eichenberger, *Helv. Chim. Acta*, **17**, 1395 (1934).

[6] Callow, *Biochem. J.*, **33**, 559 (1939).

[7] Reich and Reichstein, *Helv. Chim. Acta*, **26**, 2102 (1943).

[8] Ettlinger and Fieser, *J. Biol. Chem.*, **164**, 451 (1946).

[9] Ruzicka, Goldberg and Brüngger, *Helv. Chim. Acta*, **17**, 1389 (1934).

[10] Whitman and Schwenk, THIS JOURNAL, **68**, 1865 (1946).

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY][1]

4,4'-Dichlorodibutyl Ether and its Derivatives from Tetrahydrofuran

BY KLIEM ALEXANDER AND L. E. SCHNIEPP

Cleavage of the tetrahydrofuran ring by acyl halides to give halogen-substituted butyl esters has been reported by Goldfarb and Smorgonskii,[2] Cloke and Pilgrim[3] and Manchen and Schmidt.[4] The reaction of tetrahydrofuran with acetyl chloride, catalyzed with a small amount of anhydrous zinc chloride, gives a good yield of δ-chlorobutyl acetate plus small amounts of compounds of the formulas: $CH_3COO(CH_2)_4O(CH_2)_4Cl$ and $CH_3COO(CH_2)_4O(CH_2)_4O(CH_2)_4Cl$.[3]

Because of the apparent ease with which acyl halides cleave the hydrogenated furan ring, an investigation was undertaken to determine whether or not inorganic acid chlorides react similarly. Preliminary experiments showed that phosphorus oxychloride, thionyl chloride and silicon tetrachloride, when catalyzed with zinc or zinc chloride, reacted vigorously with tetrahydrofuran. In no case was it found possible to isolate the phosphate, sulfite, or silicate esters; however, decomposition

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Y. L. Goldfarb and L. M. Smorgonskii, *J. Gen. Chem.* (*USSR*), **8**, 1516–1522 (1938).

[3] J. B. Cloke and F. J. Pilgrim, THIS JOURNAL, **61**, 2667 (1939).

[4] F. Manchen and W. Schmidt, U. S. Patent 2,314,454 (1943).

of the reaction mixtures with water, followed by vacuum distillation of the water-insoluble products, gave a fair yield of 4,4′-dichlorodibutyl ether, a high boiling liquid which has been previously prepared from 4-chlorobutanol by Trieschmann.[5]

During these investigations a number of reports on German technical developments became available through the Office of Technical Services. Several of these reports dealt directly with the reactions under investigation. Delfs[6] in his discussion of the polymerization of alkylene oxides shows that tetrahydrofuran is readily converted to polyalkylene ethers, with chlorine end-groups, by the action of thionyl chloride catalyzed with ferric chloride. Technical development of this reaction led to the production of synthetic lubricants.[7]

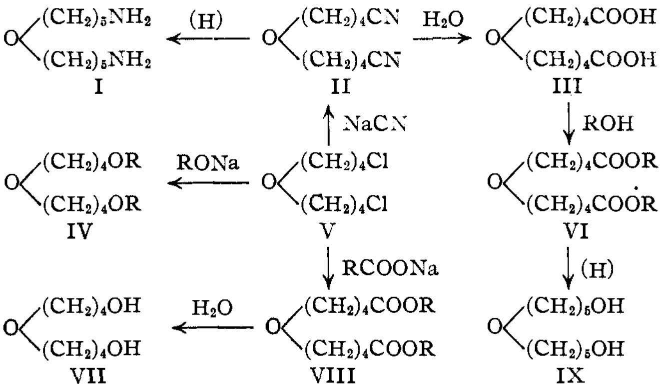
A report by Krzikalla and Maier[8] discusses the cleavage of cyclic ethers with thionyl chloride. The type of catalyst used was found to be of considerable importance. Zinc chloride favored the formation of 1,4-dichlorobutane from tetrahydrofuran, whereas with sulfuric acid as the catalyst high yields of 4,4′-dichlorodibutyl ether were obtained. The type of product was also found to be a direct function of the molar ratio of thionyl chloride to tetrahydrofuran. By varying that ratio, greater or lesser amounts of 1,4-dichlorobutane, 4,4′-dichlorodibutyl ether, and a trimeric ether of the formula $Cl(CH_2)_4O(CH_2)_4O(CH_2)_4Cl$ were obtained.

The superiority of sulfuric acid as a catalyst for the cleavage of tetrahydrofuran by phosphorus oxychloride was established in our subsequent investigations, and yields of 4,4′-dichlorodibutyl ether were improved up to 65–70% of the theoretical.

The conversion of tetrahydrofuran to 4,4′-dichlorodibutyl ether takes place by one of several possible mechanisms. Our failure to isolate chlorobutyl phosphate esters which might convert to the ether on heating, and the observed polymer formation when tetrahydrofuran was treated with thionyl chloride and ferric chloride at room temperature, indicate that the reaction is one of polymerization and depolymerization as discussed by Delfs.[6] This route of formation is also favored by the facts (1) that the high boiling residues from dichloroether distillations can be further converted to dichlorodibutyl ether by retreatment with phosphorus oxychloride, and (2) by the formation of the trimeric ether $Cl(CH_2)_4O(CH_2)_4O(CH_2)_4Cl$ when less than one-third mole of phosphorus oxychloride per mole of tetrahydrofuran is used in the reaction.

4,4′-Dichlorodibutyl ether is an interesting intermediate for the preparation of a variety of difunctional compounds. The halogens are readily replaced by cyano, alkoxy, acyloxy and similar groups. Oxydivaleric acid and its esters, 5,5′-diaminodiamyl ether, 4,4′-dihydroxydibutyl ether and 5,5′-dihydroxydiamyl ether have been prepared from such derivatives.

Derivation of these products may be illustrated as follows



Attempts to apply the same ring cleavage reaction to tetrahydropyran and tetrahydromethylfuran gave much lower yields of the expected dichlorodiamyl ethers. Tetrahydropyran apparently underwent side reactions involving dehydrohalogenation of the cleavage products and yielded a complex reaction product from which only a small yield of 5,5′-dichlorodiamyl ether could be isolated.

Experimental

4,4′-Dichlorodibutyl Ether (V).—A mixture of 72 g. (1.0 mole) of tetrahydrofuran and 51.2 g. (0.33 mole) of phosphorus oxychloride was placed in a 1-liter, three-necked flask equipped with stirrer, reflux condenser, and thermometer. The mixture was cooled in a water bath, and 10 cc. of concentrated sulfuric acid added gradually with stirring. The temperature was then slowly raised by heating in a bath. At about 80° a vigorous exothermic reaction occurred and cooling was necessary to keep the reaction under control. The temperature was controlled at 80–100° until the exothermic reaction subsided. This period usually lasted about forty minutes and was accompanied by refluxing, some evolution of hydrogen chloride, and the precipitation of a gelatinous, phosphorus-containing material. The reaction mixture was then held at 90–100° for an additional ten minutes after which 100 cc. of water was added and heating to reflux continued for thirty minutes longer.

The unchanged tetrahydrofuran and the by-product 1,4-dichlorobutane were removed by distilling their water azeotropes. The water and oil layers were separated after the residue from this distillation had cooled. The aqueous layer was extracted twice with ether, the ether and oil layers combined and water-washed. The ether was evaporated and the residue distilled under reduced pressure. The main fraction of distillate boiling at 83–87° (0.4–0.6 mm.) weighed 64.5 g. and was essentially pure 4,4′-dichlorodibutyl ether. The yield, based on tetrahydrofuran of which 5.5 g. was recovered, was 70% of the theoretical. Three grams of 1,4-dichlorobutane was isolated from the azeotropic distillates.

Refractionation of a composite of 250 g. of 4,4′-dichlorodibutyl ether gave 245 g. of a colorless, water-insoluble product having the following properties: b. p. 84–86° (0.5 mm.), d^{25}_4 1.069, n^{25}_D 1.4567. *Anal.* Calcd. for

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(5) H. G. Trieschmann, U. S. Patent 2,245,509 (1941).

(6) Delfs, P. B. 717, O. T. S., U. S. Department of Commerce.

(7) F. H. Roberts, P. B. 898, O. T. S., U. S. Department of Commerce.

(8) Krzikalla and Maier, P. B. 631, O. T. S., U. S. Department of Commerce.

$C_8H_{16}OCl_2$: C, 48.2; H, 8.09; Cl, 35.6. Found: C, 48.6; H, 7.88; Cl, 35.5. Calcd. for $Cl(CH_2)_4O(CH_2)_4Cl$: *M*D 50.52; *M*D found 50.70.

The same product was obtained in lower yields by treating tetrahydrofuran with phosphorus trichloride, thionyl chloride, phosgene, and silicon tetrachloride, all catalyzed by sulfuric acid; and with phosphorus oxychloride catalyzed by zinc, zinc chloride, aluminum chloride, ferric chloride, chlorosulfonic acid and metaphosphoric acid.

The reaction was also run in solvents such as benzene, toluene and carbon tetrachloride, but in all cases the yield was lower than by the method described.

Polymerization of Tetrahydrofuran.—Tetrahydrofuran was polymerized by the method of Delfs[6] to determine whether such a polymeric material could be converted to 4,4'-dichlorodibutyl ether.

Tetrahydrofuran was mixed with thionyl chloride and anhydrous ferric chloride in a molar ratio of 85.5:12:2.5 and allowed to stand for eleven days at room temperature, in a flask protected against entry of atmospheric moisture. Water was then added and the unchanged tetrahydrofuran recovered by distillation. The water-insoluble oil layer was separated, washed with water, and heated to 140° under vacuum (0.35 mm.). No distillate other than water was collected. From 92.5 g. of original reaction mixture 46.5 g. of a brown, oily liquid was obtained. This material solidified to a waxy solid when cooled below 0°.

Anal. Found: C, 61.4; H, 10.26; Cl, 9.60.

The chlorine value indicates a molecular weight of 739 and x equal 8.5 for a polymer of the assumed structure $Cl[(CH_2)_4O]_x\text{-}(CH_2)_4Cl$.

Anhydrous aluminum chloride used in place of ferric chloride gave a comparable product in lower yield.

A 27.4 g. sample of this polymer was heated for two and one-half hours with 14.3 g. of phosphorus oxychloride and 0.25 g. of concentrated sulfuric acid. The reaction was only mildly exothermic at about 100° and the temperature of the reaction mixture was not allowed to exceed 125°. Addition of water, separation of the water-insoluble products, and distillation gave 14 g. (40%) of 4,4'-dichlorodibutyl ether, showing that partial depolymerization occurred on heating with inorganic acid halides.

Based on this observation, 157 g. of high-boiling and polymeric residues from earlier dichlorodibutyl ether preparations was heated with 71 g. of phosphorus oxychloride and 3 cc. of concentrated sulfuric acid. Workup and distillation of this reaction mixture gave 28 g. of 1,4-dichlorobutane, 35.4 g. of 4,4'-dichlorodibutyl ether, and 6.5 g. of a higher boiling [91–155° (0.5 mm.)] material.

4,4'-Dichlorodibutyl ether is partially destroyed under such reaction conditions, 50–75% being recovered, depending upon the severity of the conditions used.

1,4-Di-(δ-chlorobutoxy)-butane.—Tetrahydrofuran, 162 g. (2.25 moles), reacted with 77 g. (0.5 mole) of phosphorus oxychloride and 3 cc. of concentrated sulfuric acid. Distillation of the water-insoluble products of the reaction gave 85 g. (42.7%) of 4,4'-dichlorodibutyl ether, 39.4 g. of a distillate collected over the range of 120–160° at 1 mm., and 18.5 g. of a viscous liquid residue. Redistillation of the higher-boiling product gave a liquid having the following properties: b. p. 133° (0.6 mm.), n^{23}D 1.4535, $d^{23}{}_4$ 1.0444.

Anal. Calcd. for $C_{12}H_{24}O_2Cl_2$: Cl, 26.15. Found: Cl, 25.9.

This product is probably $Cl(CH_2)_4O(CH_2)_4O(CH_2)_4Cl$.[8]

5,5'-Dichlorodiamyl Ether.—Tetrahydropyran, 86 g. (1 mole), was mixed with 51.2 g. (0.33 mole) of phosphorus oxychloride and 2.5 cc. of concentrated sulfuric acid and the mixture stirred and heated to reflux for twelve hours. There was no evidence of an exothermic reaction such as was observed with tetrahydrofuran. Only a very gradual increase in boiling temperature, from 80 to 112°, occurred during the heating period. Hydrogen chloride was evolved throughout the refluxing period, the amount increasing with the increase in temperature. At the end of the heating period 100 cc. of water was added to the mixture and refluxing continued for one hour. Distillation of the water-insoluble reaction products gave 18 g. of 1,5-dichloropentane, 25 g. of a yellow liquid, b. p. 96–125° (0.5–0.8 mm.), and 26 g. of residue. Refractionation of the yellow liquid fraction gave 8.8 g. of a colorless liquid, b. p. 65–70° (3–4 μ); n^{27}D 1.4580; $d^{27}{}_4$ 1.0349; *M*D calcd. for $Cl(CH_2)_5O(CH_2)_5Cl$, 59.76; *M*D found 60.05.

Anal. Calcd. for $C_{10}H_{20}OCl_2$: Cl, 31.25. Found: Cl, 31.2.

No conditions were found whereby this compound could be prepared in better than 10–15% yields.

4,4'-Dichlorodiamyl Ether.—2-Methyltetrahydrofuran, 172 g. (2.0 moles) was mixed with 102.3 g. (0.67 mole) of phosphorus oxychloride and 1.3 g. of anhydrous zinc chloride. The mixture was heated to reflux for five hours during which the temperature gradually increased from 84 to 108°. The reaction mixture was diluted with water and heated to reflux for thirty minutes. The aqueous and oil layers were separated, the oil layer washed with water, and distilled. In addition to unchanged tetrahydromethylfuran, 1,4-dichloropentane and undistillable residue, 54 g. (23.8% yield) of 4,4'-dichlorodiamyl ether boiling at 69–75° (0.3 mm.) was obtained. Redistillation of this product yielded 38 g. of material having the following properties: b. p. 94–95° (0.88 mm.); n^{25}D 1.4533; $d^{25}{}_4$ 1.0191. *M*D calcd., 59.76; found, 60.28.

Anal. Calcd. for $C_{10}H_{20}OCl_2$: C, 52.80; H, 8.87; Cl, 31.25. Found: C, 53.1; H, 8.85; Cl, 30.3.

No attempt was made to determine whether this product was a single compound or a mixture of the three possible isomeric 4,4'-dichlorodiamyl ethers.

Derivatives of 4,4'-Dichlorodibutyl Ether

4,4'-Dicyanodibutyl Ether (Oxydivaleronitrile) (II).—A mixture of 99.5 g. (0.5 mole) of 4,4'-dichlorodibutyl ether, 58 g. (1.18 moles) of pulverized sodium cyanide and 190 cc. of anhydrous methanol was charged into a steel hydrogenation bomb, shaken and heated to 150° for six hours. After the bomb had cooled, the reaction mixture was removed, filtered free of precipitated salt, and the methanol removed by evaporation on a steam-bath. The dark-colored residue was dissolved in ether, the solution filtered, and the filtrate washed with water. The ether was removed by evaporation and the residue heated to 200° at 0.7 mm. pressure. The small amount of distillate, 8 g., gave analytical and refractivity values for 4-methoxy-4'-cyanodibutyl ether.

Anal. Calcd. for $C_{10}H_{19}O_2N$: OCH_3, 16.74; N, 7.57; *M*D 51.4. Found: OCH_3, 15.75; N, 7.78; *M*D 51.6.

The undistilled material weighed 73 g., an 81% yield of oxydivaleronitrile. A sample of this dark-colored product was purified by distillation under high vacuum and had the following properties: b. p. 75–80° (10^{-4} mm.); n^{26}D 1.4453; $d^{26}{}_4$ 0.9627; *M*D calcd. 49.54; found, 49.70.

Anal. Calcd. for $C_{10}H_{16}ON_2$: C, 66.6; H, 8.95; N, 15.55. Found: C, 66.55; H, 8.82; N, 15.29.

4,4'-Dicarboxydibutyl Ether (Oxydivaleric Acid) (III).—Oxydivaleronitrile, 45 g. (0.25 mole), was hydrolyzed by refluxing for five hours with a mixture consisting of 150 cc. of alcohol, 150 cc. of water, and 40 g. of sodium hydroxide. The alcohol was removed by distillation and the aqueous alkaline solution acidified with 9 *N* sulfuric acid. The product separated as a brown, crystalline solid. The yield was 49 g. or 90% of the theoretical. This crude product was dissolved in hot water, the solution treated with activated carbon, and filtered. The product crystallized as white leaflets, m. p. 88.5–89.5°.

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31; neut. equiv., 109.1. Found: C, 55.15; H, 8.13; neut. equiv., 110.4.

Both the crude and the distilled oxydivaleronitrile gave high yields of the desired acid.

A sample of this acid when heated with hydriodic acid

TABLE I

ESTERS OF OXYDIVALERIC ACID, ROOC—$(CH_2)_4$—O—$(CH_2)_4$—COOR

R	B. p., °C.	Pres., mm.	Yield, %	$n^{25}D$	d^{25}_4	Formula	Saponification equivalent Calcd.	Found
Ethyl	117–118	0.3	90	1.4356	0.9719	$C_{14}H_{26}O_5$	137.2	136.2
n-Butyl	172–174	1.0	75	1.4405	0.9622	$C_{18}H_{34}O_5$	165.2	166.1
Tetrahydrofurfuryl	220–221	0.66	67	1.4680	1.0883	$C_{20}H_{34}O_7$	193.2	195.2

TABLE II

4,4'-DIALKOXYDIBUTYL ETHERS, R—O—$(CH_2)_4$—O—$(CH_2)_4$—O—R

R	B. p., °C.	Pres., mm.	Yield, %	$n^{25}D$	d^{25}_4	*M*D Calcd.	*M*D Found	Formula	Analyses, % C Calcd.	C Found	H Calcd.	H Found
Methyl	67	0.55	86	1.4219	0.8972	53.32	53.88	$C_{10}H_{22}O_3$	63.1	62.4	11.66	11.3
Ethyl	76–77	.45	70	1.4230	.8761	62.56	63.46	$C_{12}H_{26}O_3$	66.01	65.3	12.00	11.65
n-Butyl	114–116	.45	60	1.4304	.8687	81.04	81.17	$C_{16}H_{34}O_3$	70.02	69.8	12.49	12.3
Isoamyl	125–126	.4	75	1.4322	.8609	90.28	91.14	$C_{18}H_{38}O_3$	71.47	71.4	12.66	12.30

was converted in high yield to δ-iodovaleric acid, m. p. 56–57°.

Esterification with ethyl, *n*-butyl, and tetrahydrofurfuryl alcohols gave good yields of the normal oxydivalerates (VI). The properties of these are listed in Table I.

5,5'-Dihydroxydiamyl Ether (IX).—Diethyl oxydivalerate, 41.2 g. (0.15 mole), was reduced with sodium and alcohol by the procedure described by Manske[9] for the reduction of diethyl sebacate. The product, 20.3 g. (71% yield), had the following properties: m. p. 16–18°, b. p. 141–142° (0.5 mm.); $n^{25}D$ 1.4570; d^{25}_4 0.9727; *M*D calcd., 53.08; found, 53.26; soluble in water and ether, insoluble in benzene.

Anal. Calcd. for $C_{10}H_{22}O_3$: C, 63.18; H, 11.66. Found: C, 62.3; H, 11.8.

5,5'-Diaminodiamyl Ether (I).—Oxydivaleronitrile, 30 g. (0.166 mole), was dissolved in 350 cc. of absolute ethanol and the solution heated to boiling. Sodium, 31 g., was added in small pieces to the boiling solution over a period of forty-five minutes. Boiling was continued until all of the sodium had reacted. Most of the alcohol was then removed by distillation and the residue acidified with hydrochloric acid. The acidified mixture was evaporated to dryness and the amine hydrochloride extracted from the sodium chloride with anhydrous ethanol. Addition of ether to the alcoholic extract precipitated the diamine dihydrochloride as a white crystalline solid; yield 30.5 g., 70% of theoretical.

Anal. Calcd. for $C_{10}H_{24}ON_2·2HCl$: Cl, 27.1. Found: Cl, 27.6.

A portion of this dihydrochloride was mixed with an excess of 50% potassium hydroxide and the insoluble oil separated by extraction with ether. Evaporation of the ether left a colorless, strongly basic liquid which absorbed carbon dioxide from the air to form a stable carbonate. The free diamine had the following properties: $n^{22}D$ 1.4602; $d^{22}D$ 0.907.

Anal. Calcd. for $C_{10}H_{24}ON_2$: N, 14.87. Found: N, 14.57.

Dibenzoyl derivative, m. p. 84°. (*Anal.* Calcd.: N, 7.07. Found: N, 6.99.)

4,4'-Diacetoxydibutyl Ether (VIII).—4,4'-Dichlorodibutyl ether, 60 g. (0.3 mole), was mixed with 98 g. (1 mole) of fused potassium acetate and 60 cc. of glacial acetic acid. The mixture was refluxed for fifteen hours with occasional stirring to break up incrustations of insoluble salts. The reaction mixture was then cooled, diluted with 600 cc. of water, and the product separated by extraction with ether. Distillation of the residue from ether evaporation gave 60 g. (81% yield) of a colorless liquid, b. p. 115–118° (0.6 mm.); $n^{28}D$ 1.4330; d^{28}_4 1.018.

Anal. Calcd. for $C_{12}H_{22}O_5$: C, 58.5; H, 9.00; acetyl, 34.94; sapn. equiv., 123.1. Found: C, 58.6; H, 8.93; acetyl, 34.92; sapn. equiv., 122.7.

4,4'-Dihydroxydibutyl Ether (VII).—Methyl alcoholysis of 4,4'-diacetoxydibutyl ether gave a quantitative yield of 4,4'-dihydroxydibutyl ether, b. p. 115–116° (0.3 mm.); $n^{26}D$ 1.4544; d^{26}_4 0.9999; *M*D calcd., 43.82; found, 43.93. Di-α-naphthylurethan, m. p. 124–125° (*Anal.* Calcd.: N, 5.60. Found: N, 5.56).

4,4'-Dialkoxydibutyl Ethers (IV).—4,4'-Dichlorodibutyl ether was converted to dialkoxydibutyl ethers by refluxing for eight hours with the sodium alkoxides in solutions of the respective alcohols. These dialkoxy products were obtained in yields of 70–80% as colorless mobile liquids (see Table II).

Acknowledgment.—The tetrahydrofuran used in this investigation was generously supplied by the Electrochemicals Department, E. I. du Pont de Nemours and Company. C. H. Van Etten of this Laboratory performed the analyses.

Summary

A method is described for the conversion of tetrahydrofuran to 4,4'-dichlorodibutyl ether in 65–70% yields. Application of the method to tetrahydropyran and tetrahydromethylfuran gave poor yields of the expected dichlorodiamyl ethers.

A number of derivatives of 4,4'-dichlorodibutyl ether, not previously reported, are described.

PEORIA, ILLINOIS RECEIVED SEPTEMBER 19, 1947

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[9] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 154.