NOTES

Certain Diethers and Triethers[1]

By Lucile Liston and William M. Dehn

For the purpose of testing their solubility on cellulose esters, ethers of the types $ROCH_2CH_2OR'$ and $ROCH_2CH_2OCH_2CH_2OR'$ were prepared from monoethyl and monobutyl ethers of glycol and diethylene glycol. During their formation, distillation and storage certain decompositions were observed, hence these ethers are considered good material for study of hydrolysis. In general, quantitative yields of the ethers were not obtained; lower and higher boiling fractions than the ether itself were always obtained and such fractions were increased by repeated distillation. Also whereas the first distillations of allyl diethers gave 40–67% yields, after some months of storage, being redistilled, they decomposed energetically into other products. Some of these decompositions were of explosive violence. These and other pyrolytic decompositions will be investigated.

The ethers of glycol and diethylene glycol were converted into their sodium compounds and then were refluxed with the alkyl chloride. Advantageously comminuted sodium was prepared by refluxing toluene containing sodium in a flask on an oil-bath. The flask was then stoppered and shaken vigorously while being held by two towels. The mixture of sodium and toluene was used directly, or the toluene was displaced by petroleum ether or the hydrocarbon was practically decanted. First the glycol monoether, then the alkyl halide were added from the top of a condenser at such rates that the reactions could be controlled. After heating in an oil-bath to complete the reactions, the mixtures were either distilled directly or the contained salt was first removed by filtering or extracting with water.

	B. p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Ethylene glycol diethers						
Allyl, ethyl	139–142	60	64.59	64.65	10.84	10.83
n-Pentyl, ethyl	180–183	48	67.42	67.08	12.58	12.37
Allyl, butyl	183–184	67	68.28	68.28	11.47	11.53
n-Pentyl, butyl	221–222	43	70.16	70.59	12.85	13.07
Butyl, ethyl	164–165	90	65.69	65.44	12.43	12.39
Diethylene glycol diethers						
Allyl, ethyl	200–203	40	62.00	62.38	10.41	10.29
Butyl, ethyl	218–219	40	63.11	63.23	11.68	11.84
n-Pentyl, ethyl	121–124$_{18}$	30	64.65	64.44	11.84	11.76

Fractionations of these complex ethers gave indications of thermal decomposition, thus accounting for some of the low yields, especially in cases of the unsymmetrical complex ethers.

Ethylene glycol diethyl ether boiling at 124° was obtained in 70% yields; ethylene glycol dibutyl ether boiling at 204° was obtained in 75% yields.

Summary.—A number of new complex glycol ethers have been prepared and analyzed.[2]

(2) For other studies along this line, see Conn, Collett and Lazzell, This Journal, **54**, 4370 (1932); Cretcher and Pittenger, *ibid.*, **47**, 163 (1925).

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Received March 7, 1938

Some New Esters by Automatic Processes without Catalysts[1]

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By use of a modification of the Betz–Holden automatic water-removing trap, new esters of the chloroacetic acids were prepared in very satisfactory yields. The modification of apparatus consisted merely of a stopcock at the bottom of the graduated tube so that the calculated volume to be occupied by the water at the completion of the reaction, could be adjusted easily to reach exactly the overflow level. The advantages of this adjustment are that a visible indication of the progress of the reaction is afforded and the process can be continued to completion, or longer, without surveillance. The flask containing the acid and alcohol is connected with the water trap and the return condenser and the mixture is heated in an oil-bath for such time as is necessary to fill the trap with water to the level of overflow. At the beginning of the process, alcohol, acid, ester, and water will collect in the separator but progressively all but traces of acid and the water will flow back into the flask. With different reactions, the times necessary for heating were between one and eight hours. The products were washed with water containing sodium carbonate, dried with calcium chloride and fractionated, preferably *in vacuo*. The analyzed esters are

(1) Original manuscript received August 24, 1934.

(1) Original manuscript received June 19, 1934.