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]

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[1] Original manuscript received August 24, 1934.

[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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Some New Esters by Automatic Processes without Catalysts[1]

By Thomas R. Liston and William M. Dehn

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

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[1] Original manuscript received June 19, 1934.

Alcohol	Acid, g.	Alc., g.	Time, hrs.	% ester	B. p. 756 mm. °C.	B. p., °C.	B. p., Mm.	Sp. gr. 20°/20°	Chlorine, % Calcd.	Chlorine, % Found
				Esters of Acetic Acid						
n-Butyl	240	300	3	90	124–126					
				Esters of Monochloroacetic Acid						
n-Butyl	47	50	1.5	97		94	38			
n-Amyl	100	120	3	88	196	105	35	1.0514	21.59	21.81
s-Amyl	47	50	3	89	185	93	27	1.0475	21.59	21.65
Diethyl methyl	94	100	4	85	184	93	30	1.0469	21.59	21.62
t-Amyl	94	100	2	65	168	88	43	1.0627	21.59	21.61
				Esters of Dichloroacetic Acid						
n-Butyl	64	50	3	98		102	37			
n-Amyl	65	60	1.5	94	207	124	48	1.1455	35.63	35.52
s-Amyl	65	60	4	93	198	93	20	1.1210	35.63	35.29
Diethyl methyl	65	60	7	95	197[a]	105	40	1.1225	35.63	35.35
t-Amyl	65	60	2	75	180[a]	93	30	1.1230	35.63	35.72
				Esters of Trichloroacetic Acid						
n-Butyl	82	50	3	98		111	40			
n-Amyl	61	38	3	91	218	118	30	1.2475	45.59	45.90
s-Amyl	81	60	2.5	95	206	108	30	1.2084	45.59	45.55
Diethyl methyl	163	100	5	80	201[a]	105	25	1.2081	45.59	45.71
t-Amyl	81	60	1.5	84	191[a]	105	30	1.2505	45.59	45.73

[a] These tend to decompose partly into olefin and acid.

new; some old esters are given for comparisons of yields.

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The Relative Partial Molal Heat Content of Sodium Bromide in Aqueous Solutions at 25°

BY A. L. ROBINSON

Harned and Crawford[1] have measured recently the electromotive forces of the cells

$$\mathrm{Ag{-}AgBr/NaBr}(m)/\mathrm{Na_xHg}(m < 0.1)/\mathrm{NaBr}(0.1)/\mathrm{AgBr{-}Ag}$$

at temperatures from 0 to 40° and from these have calculated values for the relative partial molal heat contents of sodium bromide. Their $\bar{L}_2$ values at 25° may be compared with values determined from calorimetric measurements extending to 0.00016 m.[2]

m	$\bar{L}_2$, e. m. f.	$\bar{L}_2$, cal.
0.1	101	76
.2	79	56
.5	55	− 32
1.0	−211	−208
1.5	−421	−384
2.0	−587	−540
2.5	−719	−656
3.0	−819	−753
3.5	−857	−834
4.0	−887	−899

The agreement is fair although the differences are somewhat larger than the usual estimates of precision of the two methods.

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[1] H. S. Harned and C. C. Crawford, THIS JOURNAL, **59**, 1903 (1937).

[2] H. Hammerschmid and A. L. Robinson, *ibid.*, **54**, 3120 (1932).

A Sensitive Manostat for Low Gas Pressures. A Correction

BY THEODORE SOLLER, SEYMORE GOLDWASSER AND RALPH A. BEEBE

We are indebted to Professor Earl B. Working for calling our attention to the fact that the diagram of the photoelectric relay circuit given in our paper: "A Sensitive Manostat for Low Pressures and its Application to the Adsorption of Hydrogen and Deuterium on Copper,"[1] should contain a grid leak, that is, a high resistance of the order of 10^8 ohms, between the grid and the cathode of the 6C6 tube. With infinite resistance in the grid circuit, this tube would block.

We have found that under ordinary conditions of humidity, the leakage resistance of the condenser and the sockets is sufficient to prevent blocking, so it has not been necessary for us to introduce a separate resistor. But under conditions of extremely good insulation it would be necessary to introduce a separate high resistance of this order of magnitude.

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[1] THIS JOURNAL, **58**, 1703 (1936).

We thank Professor Working for calling this to our attention.

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The Action of Sodium Phenylacetylene on α,β-Unsaturated Esters

BY DAVID E. WORRALL

It has been reported[1] that esters of formic acid react with sodium phenylacetylene producing an unsaturated aldehyde. Nef,[2] however, was unable to obtain even a trace of the corresponding ketone from ethyl acetate or benzoate, although the acid chloride and anhydride gave positive results. Because of these contradictory results and because little is known concerning the activity of acetylenic salts with unsaturated systems, an investigation was made with several unsaturated esters.

It was found that phenylcinnamylacetylene is obtained readily by the interaction of sodium phenylacetylene and ethyl cinnamate the result probably of 1,2-addition followed by the elimination of sodium alcoholate. This ketone, containing as it does a double and triple bond conjugated with a carbonyl group, has interesting possibilities as a vehicle for testing the selective reactivity of reagents for such conjugate systems. Actually the accumulation of unsaturated groups appears to hinder rather than promote the normal reactivity of the carbonyl group. Attempts to force a reaction result in the formation of nontractable tars, while more powerful reagents such as the Grignard cause the ketone to act as an enol.

Experimental

Cinnamylphenylacetylene.—To 0.2 gram mole of sodium phenylacetylene suspended in dry ether and connected to a reflux condenser was added the equivalent of ethyl or methyl cinnamate. Heat sufficient to cause gentle boiling was evidenced for a few minutes. A slow but steady evolution of hydrogen took place even after long standing, due to secondary reactions. The deeply colored mixture was allowed to evaporate in a stream of air after addition to cracked ice containing a slight excess of acetic acid. The resulting oil quickly became crystalline if seeded: yield, after washing with a small volume of cold alcohol, 21 g. It separated from benzene–petroleum ether mixtures in the form of small lustrous needles melting at 140–141°.

Anal. Calcd. for $C_{17}H_{12}O$: C, 88.0; H, 5.1. Found: C, 87.9; H, 5.3.

It responded to the usual tests for unsaturation, but the addition products, with bromine for example, were obtained only as intractable mixtures. The original substance was sensitive to acids and even dilute acetic acid caused tar formation on long standing at room temperature. A purple color formed when a trace of the ketone was dissolved in cold sulfuric acid, subsequently becoming greenish-fluorescent in appearance. While more stable toward alkaline reagents, hot solutions eventually caused resinification. Traces of phenylacetylene and benzaldehyde were detected. No reactions were observed with hydroxylamine or hydrazine even after long heating. The use of higher temperatures with sealed tubes produced tars. A crystalline product quickly formed with both methyl- and phenylmagnesium halide, but on decomposition with dilute acid the original ketone was recovered. It liberated hydrogen on contact with sodium and displaced sodium from sodium phenylacetylene, thus explaining the secondary reactions observed in the original preparation. Benzoic acid and benzaldehyde were identified among the oxidation products of the ketone with permanganate. Ethyl crotonate reacted even more vigorously with sodium phenylacetylene, but the product was obtained only as a thick oil. Benzoyl methyl acrylate yielded an amorphous powder that was not further examined.

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[1] Moureu and Delage, *Compt. rend.*, **133**, 105 (1901).

[2] *Ann.*, **308**, 279 (1899).