

produced in good yield from an unsaturated hydrocarbon. Several tertiary alcohols have been isolated as the result of the ozonization of alicyclic hydrocarbons. Unsaturated hydrocarbons or ketones may be formed by the dehydration of these alcohols under rather mild conditions.

Rather high yields of acids have been formed as the result of the ozonization of saturated hydrocarbons. These experiments give striking evidence of the mildness of the conditions necessary for oxidation in alicyclic compounds.

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[CONTRIBUTION NO. 147 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

Symmetrical Dialkoxyacetones

BY HENRY R. HENZE AND BURL G. ROGERS

Although considerable attention has been given to the synthesis of keto ethers, especially of late in this Laboratory,¹ very little study seems to have been made of the preparation of dialkoxy ketones. In fact, the production of but one example of this type, namely, diethoxyacetone, is recorded in the chemical literature.

Apparently the initial synthesis of diethoxyacetone² was accomplished through hydrolysis of ethyl ethoxyacetoethoxyacetate. Subsequent investigators,³ too, with the exception of Gintl,⁴ who obtained diethoxyacetone in low yield by the destructive distillation of calcium ethoxyacetate, have used the Claisen condensation in order to prepare this substituted ketone.

Since, in connection with another problem, several dialkoxyacetones were needed, attention has been directed to the development of a general method for their preparation. The utilization of the Claisen condensation for the synthesis of *sym*-dialkoxyacetones has been studied and found to be both tedious and productive of very unsatisfactory over-all yields. Obviously, the interaction of *sym*-dichloroacetone with alcoholates should constitute a direct method of obtaining the desired series of compounds; however, such treatment invariably yielded a brown, resinous mass which could not be distilled.⁵ Finally, it was found that good yields of the substituted ketones could be obtained by the oxidation of *sym*-dialkoxypropanols. The efficacy of this method

has been tested by the successful preparation of nine *sym*-dialkoxypropanols, through interaction of *sym*-glycerol dichlorohydrin and appropriate sodium alcoholates, and their subsequent conversion to the corresponding ketones through oxidation by means of sodium dichromate and sulfuric acid.

Experimental

Preparation and *sym*-Dialkoxyacetones by the Claisen Condensation.—Five *n*-alkyl chloroacetates (methyl through amyl) required in this investigation were synthesized in 70% yield according to the method of Conrad⁶ and converted in 50% yield into the corresponding *n*-alkyl *n*-alkoxyacetates following a procedure outlined by Schreiner.⁷ In turn the alkyl alkoxyacetates were condensed to *n*-alkyl *n*-alkoxyaceto-*n*-alkoxyacetates, by means of the appropriate sodium alcoholate, and hydrolyzed by action of aqueous potassium carbonate solution. The yields of *sym*-di-*n*-alkoxyacetones were low, usually being but 10% of the theoretical. Data concern-

TABLE I
COMPOUNDS AND PROPERTIES

Compound	<i>n</i> -Amyl chloroacetate	<i>n</i> -Butyl <i>n</i> -butoxyacetate	<i>n</i> -Amyl <i>n</i> -amoxyacetate
Yield, %	68	61	34
B. p. corr. { °C.	198-199	123-123.5	148-149
{ mm.	744	30	35
d_{20}^{20}	1.0461	0.9214	0.9112
n_D^{20}	1.4335	1.4204	1.4284
γ^{20} , dynes/cm. ^a	28.03	26.01	26.96
MR {	Calcd.	51.68	60.91
	Found	40.96	51.72
P {	Calcd. ^b	370.2	470.0
	Found	361.9	461.2
Free surface energy, ergs	816.1	914.7	1023.2

^a Surface tensions were determined at 20° by means of a Cassel precision capillaritymeter, *Chem. Ztg.*, **53**, 479 (1929).

^b Summation values of the atomic parachor values of Sugden, *J. Chem. Soc.*, **125**, 1180 (1924).

(6) Conrad, *Ann.*, **188**, 218 (1877).

(7) Schreiner, *ibid.*, **197**, 8 (1879).

(1) THIS JOURNAL, **56**, 1350 (1934); *ibid.*, **59**, 540 (1937); *J. Org. Chem.*, **2**, 508 (1938).

(2) Grimaux and Lefèvre, *Bull. soc. chim.*, [3] **1**, 11 (1889).

(3) Erlenbach, *Ann.*, **269**, 30 (1892); Darzens and Meyer, *Compt. rend.*, **198**, 478 (1934).

(4) Gintl, *Monatsh.*, **15**, 805 (1894).

(5) It is of interest to note that Grimaux and Lefèvre (ref. 2) reported that they were unable to effect the synthesis of *sym*-diethoxyacetone by interaction of sodium ethylate and *sym*-dichloroacetone. Although reaction occurred, they obtained only resinous material.

TABLE II
sym-DIALKOXYPROPANOLS DERIVED FROM *sym*-GLYCEROL DICHLOROHYDRIN

Compound	B. p. °C. (corr.)	Mm.	d^{20}_4	n^{20}_D	γ^{20} , dynes	Yield, %	Mol. refraction		ΔMR	Parachor		ΔP	Free surface energy ergs	Carbon, %		Hydrogen, %	
							Calcd.	Found		Calcd.	Found			Calcd.	Found	Calcd.	Found
$(CH_3OCH_2)_2CHOH$	65.5-66.0	9	1.0085	1.4192	30.36	60.0	30.10	30.10	0.00	289.2	279.8	-9.4	734.9	49.96	50.11	10.07	10.09
$(C_2H_5OCH_2)_2CHOH$	61.5-62.0	2	0.9514	1.4200	27.26	46.0	39.34	39.40	+ .06	367.2	356.5	-10.7	789.0	56.71	56.96	10.89	10.86
$(n-C_3H_7OCH_2)_2CHOH$	82.0-83.0	2	.9265	1.4256	27.04	42.0	48.57	48.68	+ .11	445.2	433.5	-11.7	894.0	61.31	61.61	11.44	11.56
$(s-C_3H_7OCH_2)_2CHOH$	74.0-75.0	2	.9140	1.4185	24.54	23.0	48.57	48.62	- .05	445.2	429.0	-15.2	818.8	61.31	61.35	11.44	11.26
$(n-C_4H_9OCH_2)_2CHOH$	104.0-105.0	2	.9129	1.4302	26.84	38.0	57.81	57.81	.00	523.2	510.0	-13.2	988.9	64.65	64.57	11.85	11.97
$(i-C_4H_9OCH_2)_2CHOH$	105.0-105.5	4	.9030	1.4245	24.68	31.0	57.81	57.76	- .05	523.2	504.0	-19.2	915.9	64.65	64.42	11.85	11.69
$(s-C_4H_9OCH_2)_2CHOH$	95.0-96.0	2	.9112	1.4279	25.84	16.0	57.81	57.64	- .17	523.2	505.2	-18.0	953.5	64.65	64.92	11.85	11.72
$(n-C_5H_{11}OCH_2)_2CHOH$	124.0-125.0	2	.9045	1.4360	26.95	55.0	67.05	67.12	+ .07	601.2	585.4	-15.8	1088.7	67.18	67.34	12.15	12.02
$(i-C_5H_{11}OCH_2)_2CHOH$	125.0-126.0	2	.8985	1.4334	25.36	42.0	67.05	67.23	+ .18	601.2	580.0	-21.2	1029.0	67.18	67.45	12.15	11.93

 TABLE III
sym-DIALKOXYACETONES

Compound	B. p. °C. (corr.)	Mm.	d^{20}_4	n^{20}_D	γ^{20} , dynes	Yield, %	Mol. refraction		ΔMR	Parachor		ΔP	Free surface energy, ergs	Carbon, %		Hydrogen, %	
							Calcd.	Found		Calcd.	Found			Calcd.	Found	Calcd.	Found
$(CH_3OCH_2)_2CO$	78.0-78.5	18	1.0415	1.4174	32.57	45.0	28.59	28.54	-0.05	278.2	270.9	-7.3	763.1	50.81	50.51	8.54	8.57
$(C_2H_5OCH_2)_2CO$	105.0-105.5	35	0.9719	1.4202	28.14	67.0	37.82	38.05	+ .23	356.2	346.3	-9.9	795.8	57.49	57.55	9.66	9.78
$(n-C_3H_7OCH_2)_2CO$	124.0-125.0	28	.9452	1.4240	27.09	61.0	47.06	47.02	- .04	434.2	420.4	-13.8	877.3	62.02	62.15	10.42	10.47
$(s-C_3H_7OCH_2)_2CO$	75.0-76.5	1	.9282	1.4180	25.50	38.0	47.06	47.28	+ .22	434.2	426.2	-8.0	838.6	62.02	62.29	10.42	10.33
$(n-C_4H_9OCH_2)_2CO$	111.5-112.5	3	.9302	1.4306	27.18	66.0	56.30	56.22	- .08	512.2	496.3	-15.9	982.5	65.29	65.27	10.97	10.88
$(i-C_4H_9OCH_2)_2CO$	91.0-93.0	1	.9169	1.4236	25.19	58.0	56.30	56.22	- .08	512.2	494.0	-18.2	935.7	65.29	65.17	10.97	11.14
$(s-C_4H_9OCH_2)_2CO$	88.0-90.5	1	.9219	1.4264	26.47	30.0	56.30	56.24	- .06	512.2	497.0	-14.8	962.6	65.29	65.09	10.97	10.96
$(n-C_5H_{11}OCH_2)_2CO$	128.0-129.5	1	.9187	1.4344	27.35	70.0	65.53	65.31	- .22	590.2	573.1	-17.1	1087.0	67.76	67.96	11.38	11.28
$(i-C_5H_{11}OCH_2)_2CO$	120.0-122.0	1	.9103	1.4312	25.76	63.0	65.53	65.49	- .04	590.2	569.7	-20.5	1030.3	67.76	67.95	11.38	11.24

ing selected physical properties and analytical results are listed in Table I for three new esters synthesized in this portion of the study.

Preparation of *sym*-Dialkoxypropanols.—To at least 500 cc. of an appropriate alcohol, contained in a flask provided with a reflux condenser and a mercury-sealed mechanical stirrer, one gram atom of sodium was added in small pieces. In the case of the higher members of the series, more alcohol was added as needed to effect the solution of the metal. After cooling the solution to room temperature, one-half mole of *sym*-glycerol dichlorohydrin was added dropwise; almost immediately a precipitate of sodium chloride formed. Stirring was continued for an hour and then the sodium chloride was removed by suction filtration. The excess of alcohol was eliminated by distillation, and the *sym*-dialkoxypropanols were fractionated through an eight-inch (20-cm.), indented, reflux column. The propanols were redistilled under diminished pressure before determination of their physical properties and preceding their analysis; these data are listed in Table II. An average yield of 40% of the theoretical was obtained.

The preparation of *sym*-di-*t*-butoxypropanol was attempted unsuccessfully by the following methods: (1) interaction of sodium *t*-butylate and *sym*-glycerol dichlorohydrin; (2) interaction of *t*-butyl alcohol, epichlorohydrin and sodium hydroxide; (3) interaction of *t*-butyl alcohol, epichlorohydrin and sulfuric acid, with subsequent treatment with sodium hydroxide solution;⁸ (4) interaction of *t*-butyl alcohol, *sym*-glycerol dichlorohydrin and sodium hydroxide.¹¹ The values for physical

(8) Reboul, *Ann. chim. phys.*, **60**, 5 (1860), reported the preparation of *sym*-diethoxy- and *sym*-diisomamxypropanols by this method. No physical data were listed for the ethoxy compound; for the isomamxy derivative the following data were recorded: b. p. 272-274°; d^{20}_4 0.907.

(9) Zanino, *Atti accad. Lincei*, [3] **6**, II, 348 (1897), reported the production of *sym*-di-*t*-butoxypropanol by this method and listed b. p. 209-210°; d^{20}_4 0.921. These data are higher than the corresponding ones for the *n*-butoxy compound; in our experience with keto ethers the boiling point and density of the compounds of normal structure are higher than those of their isomers of branched structure.

(10) Fairbairne, Gibson and Stephens, *J. Chem. Soc.*, 1965 (1932), utilized this procedure in preparing *sym*-diethoxypropanol.

(11) *Ibid.*, 445 (1931); used in producing the methoxy member of the series.

properties of *sym*-diethoxypropanol did not agree well with those reported by Berthelot¹² for this compound; likewise data listed by Zunino⁹ for the dimethoxy-, di-*n*-propoxy-, di-*s*-propoxy- and diisoamoxy derivatives did not check closely with the values determined for these compounds in this investigation. However, excellent agreement was found with the data listed by Fairbourne, Gibson and Stephens^{10,11} for boiling points, densities and indices of refraction of the dimethoxy-, diethoxy-, di-*n*-propoxy- and di-*s*-propoxypropanols.

Preparation of *sym*-Dialkoxyacetones.—The *sym*-dialkoxypropanols were converted into the *sym*-dialkoxyacetones by using a procedure adapted from "Organic Syntheses."¹³ The calculated amounts of commercial grade sodium dichromate and *sym*-dialkoxypropanol were placed in a flask provided with a mechanical stirrer and maintained by cooling at 15–20° during the time of reaction. The required amount of concd. sulfuric acid, diluted one to five with water, was added slowly over a period of about four hours, but the stirring was continued for sixteen to eighteen hours. In cases in which marked thickening of the oxidation mixture was noted, water was added until the mixture could be stirred more easily. Finally, enough water was added to dissolve any chromium salt that had separated from solution; then the solution was extracted with three 75-cc. portions of ether. The ethereal extracts were treated with 25 cc. of 0.1 *N* sodium hydroxide solution and washed with three 50-cc. portions of water. The ether was removed and the ketones fractionated through efficient indented columns. The data for physical properties and analyses of the nine *sym*-dialkoxyacetones prepared are listed in Table III. Semi-

(12) Berthelot, *Ann.*, **92**, 303 (1854), recorded b. p. 190–191°; *d*₄²⁰ 0.920.

(13) Conant and Quayle, "Organic Syntheses," John Wiley & Sons, Inc., New York, N. Y., Vol. II, 1922, p. 13.

carbazones were prepared from the diethoxy-, di-*n*-propoxy-, and di-*n*-butoxyacetones; certain data for their physical characteristics and for the analyses for their nitrogen content appear in Table IV. Failure to obtain a semicarbazone from dimethoxyacetone may be attributed to its solubility; the 2,4-dinitrophenylhydrazone was employed to aid in characterization of this ketone. However, failure to obtain solid derivatives from the ketones of branched alkyl structure may be attributed to steric hindrance.

TABLE IV
SEMICARBAZONES OF *sym*-DIALKOXYACETONES,

—R	M. p., °C. (corr.)	Nitrogen, %	
		Calcd.	Found
CH ₃ ^a	119.5–120.5	18.79	18.64
C ₂ H ₅	90.0–91.0	20.69	20.59
<i>n</i> -C ₃ H ₇	85.5–87.0	18.18	18.26
<i>n</i> -C ₄ H ₉	82.5–83.5	16.22	16.50

^a These data are for the 2,4-dinitrophenylhydrazone of *sym*-dimethoxyacetone.

Summary

1. The synthesis of *sym*-dialkoxyacetones by conversion of *sym*-glycerol dichlorohydrin into *sym*-dialkoxypropanols and subsequent oxidation of the latter is very much less tedious and productive of better yields than is their preparation from alkyl alkoxyacetates by means of the Claisen condensation.

2. Nine *sym*-dialkoxyacetones have been prepared and adequately characterized.

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Bromotrichloromethane and Iodotrichloromethane

By J. H. SIMONS, T. K. SLOAT AND A. C. MEUNIER

Compounds of the halogens with carbon are of increasing interest, but in regard to some of them very little information is available in the literature. A new method of synthesis of bromo- and iodotrichloromethane has been found and studied, and attempts have been made to cause these compounds to perform the Grignard reaction. A new method of making trichloroacetyl bromide has been employed, and a way has been found of preparing anhydrous sodium trichloroacetate that has not been reported previously.

The published methods of preparing bromotrichloromethane are: a sealed tube reaction of

chloroform with bromine,¹ by the reaction of carbon tetrachloride with aluminum tribromide,² by the action of sodium hypobromite with chloroform,³ and by the reaction of potassium trichloroacetate with bromine in a sealed tube.⁴ Iodotrichloromethane has been made previously by similar methods.^{3,5}

(1) Paternò, *Jahr.*, 300 (1872); Friedel and Silva, *Bull. soc. chim.*, **17**, 538 (1872); Lecompte, Volklinger and Tchakirian, *Compt. rend.*, **204**, 1927 (1937).

(2) Vesper and Rollefson, *THIS JOURNAL*, **56**, 1455 (1934).

(3) Dehn, *ibid.*, **31**, 1225 (1909).

(4) Van't Hoff, *Ber.*, **10**, 678 (1877); Wouters, *Bull. sci. acad. roy. Belg.*, **20**, 782 (1934).

(5) Besson, *Bull. soc. chim.*, [3] **9**, 175 (1880).