

## INVESTIGATIONS IN THE FIELD OF DIOLS AND CYCLIC ETHERS. IV

### Preparation of 2-monosubstituted derivatives of trimethylene oxide

by M. BARTÓK and A. S. GILDE

Institute of Organic Chemistry, József Attila University, Szeged

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The authors have reviewed the literature of syntheses of 2-monosubstituted four-membered cyclic ethers. The syntheses of 2-methyl, 2-ethyl, 2-n-propyl, 2-phenyl and recently 2-n-butyl, 2-t-butyl, 2-c-hexyl and 2-benzyl oxetanes have been realized. It has been stated that these cyclic ethers can be prepared with a relatively good yield (mean 70%) from chloroacetates containing the corresponding primary chlorine.

The previous communication [1] dealt with the synthesis, the physical and physico-chemical properties and structure of trimethylene oxide. The present subject of the paper is the synthesis of 2-alkyl, 2-cycloalkyl and 2-aryl derivatives of trimethylene oxide.

There are two ways for synthesizing 2-monosubstituted oxetanes as regard to the preparation of starting substances and the method of ring closure:

1. The method starting from 1,3-diols, and
2. Synthesis starting from 1,3-chlorohydrins and chloroacetates, respectively.

1. After a thorough examination of literature we can state that so far experiments to synthesize four-membered cyclic ethers were undertaken in three directions:

*a)* Several investigators have dealt with the intramolecular dehydratation of 1,3-diols, however, most of the experiments failed to lead to trimethylene oxide and to its substituted derivatives [e. g. 2, 3, 4, 5]. The dehydration was effected under different conditions. Attempts to dehydrate 1,3-diols in the gaseous phase, in the presence of different catalysts, are in progress in the Institute of Organic Chemistry of the University of Szeged, too. To prepare oxetanes a new method was described by SCHMOYER and CASE [6, 7], who started from 1,3-diols. This process cannot be regarded as a pure intramolecular dehydration.

*b)* Oxetanes could be prepared by the catalytic pyrolysis of cyclic carbonates of the corresponding substituted 1,3-diols. This method was applied with success only in the synthesis of 3,3-disubstituted trimethylene oxides [8]. Of the 2-substituted oxetanes the method gained application only for the synthesis of methyl derivatives and according to the infrared spectrum of the crude product it gave a very low yield (15%).

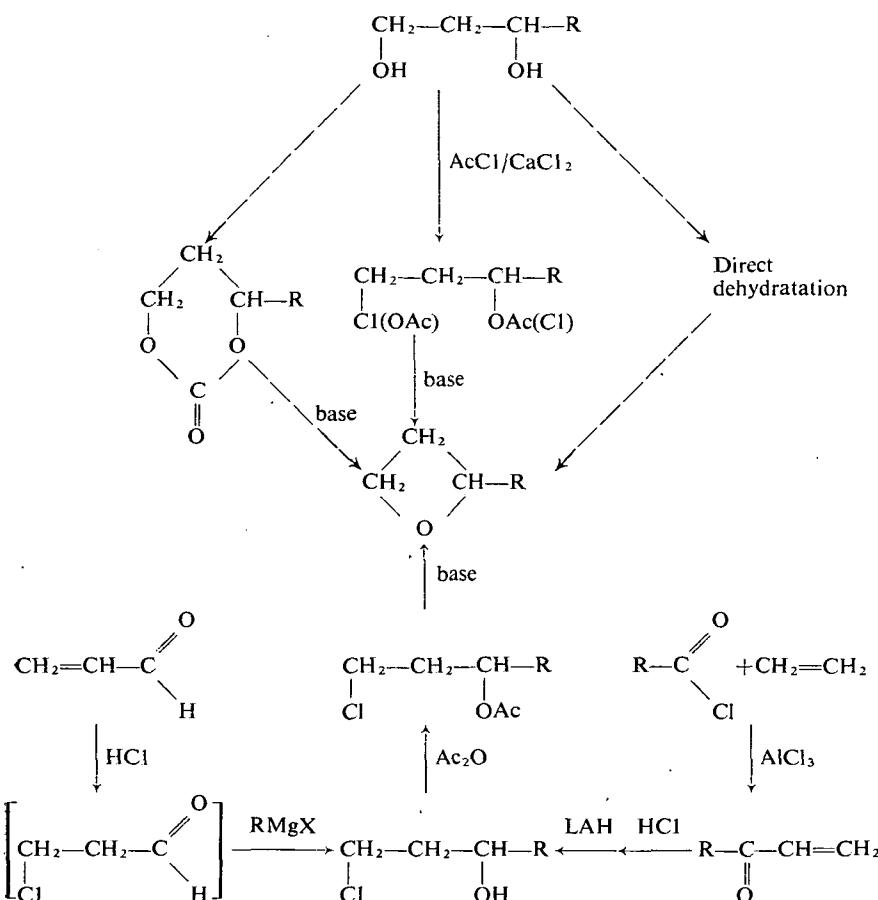
*c)* The corresponding four-membered cyclic ether could be prepared from 1,3-diols through chloroacetate too. This method is connected with the second one.

The method was applied only for 2-methyloxetane [9, 10]. We shall extend this to the synthesis of 2-monosubstituted oxetanes, a report of which will be published later. The general way of synthesis is as follows: preparation of the corresponding 1,3-diol in the simplest way (*e. g.* by the GRIGNARD reaction of  $\beta$ -oxypropionaldehyde, or by the REFORMATSKII reaction or by the PRINS reaction) from which chloroacetate is prepared in one step and the alkaline ring closure of the latter results in the formation corresponding oxetanes.

2. On the basis of experiments so far carried out, 2-substituted oxetanes were prepared with the best yield by alkaline ring closure starting from 1-R-3-chloropropanol-1, where R = alkyl and aryl, resp. The literature reports the syntheses of the following 2-substituted four-membered cyclic ethers: 2-methyloxetane [11, 12, 13, 14, 15], 2-ethyloxetane [16, 14, 15], 2-n-propyloxetane [14], 2-phenyloxetane [15].

Possibilities rendered by the synthesis are shown in Table I.

Table I.  
Preparation of 2-R-oxetanes



In the following we examine somewhat more extensively data of the literature regarding the preparation of 2-monosubstituted oxetanes. The first method will be the subject of another publication, thus this time we do not go into details only wish to turn attention to the possibilities to synthesize alkyl and aryl, respectively, 1-substituted derivatives of 1,3-propanediol.  $\beta$ -oxypropionaldehyde [17, 18, 19, 20] and some aldehydes, easy to obtain, could serve as starting materials of the synthesis. The required 1,3-diol can be obtained from the former by the GRIGNARD reaction and from the latter from  $\beta$ -oxycarbonic acid, prepared either by a reaction with ketene or by the REFORMATSKII synthesis [21]. 1,3-butanediol is a commercial prepartate (CHEMISCHE WERKE HÜLS, BDH, LIGHT's). Previously it has been mentioned that to synthesize 2-monosubstituted oxetanes, literature mostly mentions the application of chlorohydrins and chloroacetates, respectively, containing primary chlorine atom. When in the chlorohydrin molecule the chlorine atom is connected to a secondary carbon atom, under the conditions of alkaline ring closure the transformations does not result in formation of oxetane (a detailed study of these reactions is in progress). Chlorohydrins containing primary chlorine atom are easy to prepare from acrolein. From the latter compound  $\beta$ -chloropropionaldehyde is formed under anhydrous conditions, below  $-10^{\circ}\text{C}$ , on effect of hydrochloric acid, and from it the required chlorohydrin can be prepared with alkyl magnesium halides. The acrolein and hydrochloric addition was studied first by ADAM, CARTMELL, GEUTHER and GRIMAUX [22, 23]. The reaction has been dealt with more recently, too; it received manyfold application in the syntheses [24, 25, 26, 27, 28, 29, 30, 31, 16, 32, 14, 13]. The addition of hydrochloric acid, owing to the electron attractive effect of the carbonyl group, is contrasted to the MARKOWNIKOFF empiric rule [33]. Starting from acrolein, chlorohydrins can be prepared in about 30% yield. (The reason of this relative low yield is the rapid polymerisation of  $\beta$ -chloropropionaldehyde on temperature higher than  $-10^{\circ}\text{C}$  it easily trimerizes). Therefore the GRIGNARD reaction must be carried out immediately after the addition of hydrochloric acid without the isolation of  $\beta$ -chloropropionaldehyde. Literature contains the following syntheses of chlorohydrins: 1-methyl [30, 14, 13]; 1-ethyl-[29, 30, 16, 14]; 1-n-propyl-[29, 30, 14]; 1-i-propyl-[14] and 1-i-amyl-3-chloropropanol-1 [29].

Chlorohydrins containing primary chlorine atom are easy to prepare from  $\alpha$ ,  $\beta$ -unsaturated ketones, obtained by the reaction of the corresponding acid chlorides with ethylene on effect of  $\text{AlCl}_3$  or  $\text{SnCl}_4$ . On effect of hydrogen chloride the latter can be converted in to  $\beta$ -chloroethyl-alkyl and aryl ketones, respectively, and from them chlorohydrins are formed by reduction with  $\text{LiAlH}_4$ . The first step of the process can be directed so that immediately  $\beta$ -chloroethyl-alkyl and aryl, ketones are formed. The reaction between acid chlorides and olefines, on effect of metal chlorides above mentioned, was first described by BLANC and KRAPIVIN [34, 35]. If the corresponding acid chlorides are available, instead of starting from acrolein, this method can be applied with success because of the very good yield. There is a special method to prepare  $\beta$ -chloroethyl-phenyl-ketone, when it is synthesizing it from  $\beta$ -chloropropionyl chloride and benzene by the FRIEDEL-CRAFTS reaction [36, 37, 38, 39]. There are descriptions in the literature for the syntheses of the following  $\beta$ -chloroethyl-alkyl and aryl ketones, starting from acid chlorides: methyl- [40, 41, 42, 12]; ethyl- [40, 41, 32, 15]; n-propyl- [40, 41]; n-butyl- [40, 41]; and phenyl  $\beta$ -chloroethyl ketones [43, 44, 45]. The reaction of olefines and acid chlorides

on effect of  $\text{AlCl}_3$  is dealt with by THOMAS in his book published in 1941 [46]. Other methods are also available for the syntheses of  $\beta$ -chloroketones. E. G.  $\beta$ -chloroketones were prepared by the reaction of  $\beta$ -chloropropionyl chloride with organic zinc compounds [47] and by the chloromethylation of ketones in the presence of zinc chloride [48].

For the reduction of  $\beta$ -chloroketones by which we can get to the corresponding 1,3-chlorohydrins. SONDHEIMER, SEARLES and their coworkers gave descriptions [12, 15].

3-monosubstituted oxetanes are prepared by alkaline ring closure of the acetylated products of chlorohydrins mentioned above. In this respect we can find exceptions in the literature. Namely FORSBERG [14] synthesized oxetanes direct by the alkaline reaction of chlorohydrins. Using this was as Table II indicates the yield of cyclic ethers is lower than starting from chloroacetates. The mechanism of these conversions will be described in a following paper.

Now we wish to give a short review of the literature on the preparation of 2-monosubstituted oxetanes.

The first description of a synthesis of 2-methyloxetane is given in a patent [11]. 1-chlorobutanol-3 was prepared from 1,3-butanediol — (we are of the opinion that as a result of the reaction of 1,3-butanediol with hydrochloric acid, 3-chlorobutanol also forms) — which was closed to a ring in the presence of sodium hydroxide. FORSBERG [14] has prepared 2-methyloxetane from 1-chlorobutanol-3, obtained from acrolein. GAYLORD and his coworkers [13] followed a similar, method however, carried out the ring closure of chloroacetates obtained by the acetylation of chlorohydrins. 2-methyl-trimethylene oxide was prepared also from mixtures of chloroacetate obtained by the reaction of 1,3-butanediol with acetylchloride [9, 10]. The same compound was prepared from  $\beta$ -chloroethyl-methyl ketone received by the reaction of acetyl chloride and ethylene in the presence of aluminum chloride [12, 15]. The formation of cyclic ether was observed also in the catalytic decomposition of 4-methyl-1,3-dioxan-2-on but this method, owing to the low yield, cannot be regarded as the proper way of synthesizing 2-methyloxetane. SCHMOYER and CASE [7] in their new method prepared 2-methyl-trimethylene oxide direct from 1,3-butanediol, so that concentrated sulphuric acid solution of diol was added dropwise to boiling alkali.

In literature we can find three descriptions of the preparation of 2-ethyltrimethylene oxide. LESPIEAU [16] started from acrolein through chlorohydrin and chloroacetate, FORSBERG [14] followed a similar method but he started from chlorohydrin, SEARLES and his coworkers [15] prepared 2-ethyloxetane from chloroketone obtained from the reaction of  $\beta$ -chloropropionyl chloride with ethylene in the presence of aluminum chloride, via chloroacetate.

2-n-propyl and i-propyloxetanes were prepared by FORSBERG [14] by alkaline ring closure of chlorohydrins, obtained from acrolein.

The synthesis of 2-phenyltrimethylene oxide was undertaken by SEARLES and his coworkers [15].  $\beta$ -chloroketone, the starting material was prepared by the FRIEDEL—CRAFTS reaction [39]. They converted chloroketone to chlorohydrin and to chloroacetate, and by the alkaline ring closure of the latter 2-phenyloxetane was obtained. This step was also carried out direct by with chlorohydrin, but the yield was lower.

Data in literature on the % yield of 2-monosubstituted oxetanes and the starting materials of the different syntheses are summarized in Table II.

In the course of our researches of the cyclic ethers, we are dealing with the syntheses, study of the mechanism of the formations, and chemical transformations of trimethylene oxide derivatives. So far we have prepared 2-methyl-, ethyl-, n-propyl-, i-propyl-, n-butyl-, t-butyl-, c-hexyl-, phenyl-, and benzyl-oxetanes. 2-methyl-trimethylene oxide was prepared by an alkaline ring closure (as described by SEARLES and coworkers [10]) with a yield of 50% of chloroacetates obtained by MELTZER and KING's method [49] from 1,3-butanediol. At the same time we repeated SONDHEIMER's [12], further GAYLORD and his coworkers' [13] methods. Here the yield

Table II.  
Yield in per cent of

No	R	R—CH—CH <sub>2</sub> —CH <sub>2</sub> ,		R—CH—CH <sub>2</sub> —CH <sub>2</sub>		CH <sub>2</sub> —CH—R		Ref.
		OH	Cl	OAc	Cl	CH <sub>2</sub> —CH—R	CH <sub>2</sub> —O	
		Yield %		Yield %		Yield %		
		a	b	a	b	a	b	
1	methyl	— <sup>f</sup>				20		11
2	methyl	79 <sup>d</sup>	76	95	92	66	62	12
3	methyl	33	31	83	80	68	60	13
4	methyl	~16				35		14
5	methyl			70 <sup>c</sup>		42		9
6	methyl	— <sup>f</sup>		— <sup>f</sup>		55		15
7	methyl			83 <sup>c</sup>	84	52	50	10
8	methyl					~21		7
9	methyl					15		8
10	ethyl	— <sup>f</sup>	31	— <sup>f</sup>	86	— <sup>f</sup>	62	16
11	ethyl	~27				51		14
12	ethyl	71		96		60		15
13	<i>n</i> -propyl	~21	34		83	46	62	14
14	<i>i</i> -propyl	~23	33		85	48	63	14
15	<i>n</i> -butyl		30		85		85	
16	<i>t</i> -butyl		28		87		74	
17	<i>c</i> -hexyl		40		85		75	
18	phenyl	87 <sup>e</sup>	85	83	81	70	70	15
19	phenyl	87 <sup>e</sup>				58		15
20	phenyl		30		80		68	
21	benzyl		26		80		68	

*a* data in literature

*b* data in Experimental of this paper

*c* mixture of two isomers of chloroacetate

*d* yield of chloroketone was 61%

*e* yield of chloroketone was 93%

*f* yield % was not given by the authors

*g* vacant places — the authors did not deal with the synthesis of the compound

was 62 and 60%, respectively. The syntheses of all other 2-substituted oxetane derivatives were carried out starting from acrolein, according to the method already mentioned, by alkaline ring closure of the corresponding chloroacetates. 2-phenyl-trimethylene oxide was also prepared starting from phenylvinyl ketone. Table II gives the yields of the subsequent steps of the syntheses as compared with data available in the literature. These data show that the yield of cyclic ether, as a rule, is above 60%. From the yields obtained with compounds having increasing substituents at the 2-position unequivocal deductions cannot be made. We think that a more exact evaluation will be possible from results of kinetic investigations. The main reaction is accompanied by other by — reactions and the conversion, is followed by secondary processes too. These processes will be discussed in our paper dealing with the mechanism of alkaline reactions of 1,3-chlorohydrins and 1,3-chloroacetates.

### Experimental

Table III summarizes physical constants of chlorohydrins, chloroacetates and oxetanes, mentioned in the paper.

Tables IV, V and VI show the physical constants and results of mikroanalysis of the compounds described in *Experimental*.

Synthesis of 3-chloro-1-butylacetate and 4-chloro-2-butyl-acetate isomers were carried out according to MELTZER and KING [49]. The reaction mixture was cooled with ice and NaCl. Acetyl chloride was added during a period of about 3 hours and the temperature was raised to 20°C. The mixture of the two isomers was prepared from 1000 g 1,3-butanediol in 84% yield.

Boiling point 75—7°C (18 mm).

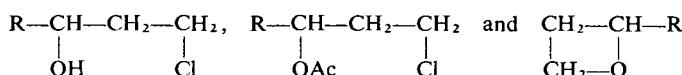
Analysis: Calculated for  $C_6H_{11}O_2Cl$

C: 47,85	H: 7,36	Cl: 23,54
Found: C: 47,76	H: 7,28	Cl: 23,60.

*4-chloro-butanon-2.* The synthesis was carried out by [12]. Ethylene was prepared by dehydration of ethylalcohol on  $\gamma$ -aluminum oxide at 400°C. From the reactor, after cooling with ice, a mixture of vapour and gas was bubbled through sodium hydroxide solution, concentrated sulphuric acid and heated calcium chloride, and then it was introduced to the reaction mixture. After corresponding purification the crude product was fractionated. Yield: 386 g (56%). B. p. 60°C (28 mm);  $n_D^{26}$ : 1,4298 (reported (12) b. p. 47°C (16 mm);  $n_D^{27}$ : 1,4299).

*$\beta$ -chloropropionaldehyde.* A calculated amount of hydrogen chloride (100 g) bubbled through concentrated sulphuric acid and dry calcium chloride was introduced into 200 ml abs. etheric solution of 168 g acrolein (3 mole) with vigorous stirring, below —10°C. The cooling is realised with a dry ice-aceton mixture, or if it is not possible, with ice and NaCl. Working with this latter, during the introduction of hydrogen chloride depending on the insulation of the bottle containing the cooling mixture and the on amount of the latter, the ice salt mixture must be changed two-four times. With effective cooling the introduction of hydrogen chloride requires two-three hours. After the absorption of the gas in the required quantity, the etheric solution is mixed continuously with 20—20 g of dry sodium carbonate and calcium

Table III.  
Data on the physical constants of



No	R	Name	Boiling point		d gr/cm <sup>3</sup>	$n_D$ (t°)	Ref.
			C°	(Hg mm)			
1.	methyl	4-chloro-butanol-2	67	(20)	—	1,4408 (26)	12
2.	methyl	4-chloro-butanol-2	63,7—64	(15)	1,0686 <sup>20</sup>	1,4430 (20)	14
3.	methyl	4-chloro-butanol-2	61	(10)	—	1,4440 (20)	10
4.	methyl	4-chloro-2-butyl-acetate	70	(16)	—	1,4260 (25)	12
5.	methyl	4-chloro-2-butyl-acetate	71—2	(16)	—	1,4273 (20)	10
6.	methyl	2-methyloxetane	59,4—7	(736)	0,8480 <sup>20</sup>	1,3889 (20)	11
7.	methyl	2-methyloxetane	60	(747)	—	1,3890 (25)	51
8.	methyl	2-methyloxetane	60—61	(762)	—	1,3894 (25)	12
9.	methyl	2-methyloxetane	59—60	—	—	1,3886 (25)	13
10.	methyl	2-methyloxetane	60—60,5	(756)	0,8494 <sup>20</sup>	1,3910 (20)	14
11.	methyl	2-methyloxetane	59,7—8	—	—	1,3919 (20)	9
12.	methyl	2-methyloxetane	59	—	—	1,3913 (20)	15
13.	methyl	2-methyloxetane	60	—	—	1,3913 (20)	10
14.	methyl	2-methyloxetane	58—61	—	—	—	7
15.	ethyl	1-chloro-pentanol-3	77—77,5	(20)	1,0327 <sup>25</sup>	1,448 (20)	16
16.	ethyl	1-chloro-pentanol-3	77,3—77,9	(17,5)	1,0427 <sup>20</sup>	1,4482 (20)	14
17.	ethyl	1-chloro-pentanol-3	82	(25)	—	1,4435 (20)	15
18.	ethyl	1-chloro-3-acetoxy-pentane	81	(13)	1,03896 <sup>24</sup>	1,431 (24)	16
19.	ethyl	1-chloro-3-acetoxy-pentane	82—4	(20)	—	1,4310 (20)	15
20.	ethyl	2-ethyloxetane	88,5—89	(748)	0,8481 <sup>20</sup>	1,4072 (20)	16
21.	ethyl	2-ethyloxetane	78,9	(759)	0,8483 <sup>20</sup>	1,4000 (20)	14
22.	ethyl	2-ethyloxetane	87	(730)	0,850	1,4040 (20)	15
23.	n-propyl	1-chlorohexanole-3	78,8—79,2	(9)	1,0132 <sup>24</sup>	1,4488 (20)	14
24.	n-propyl	2-n-propyloxetane	108—9	—	0,8494 <sup>20</sup>	1,4112 (20)	14
25.	i-propyl	1-chloro-4-methyl-pentanol-3	72,8—74,0	(10,5)	1,0233 <sup>20</sup>	1,4510 (20)	14
26.	i-propyl	2-i-propyloxetane	91,5—92	(753)	0,8480 <sup>24</sup>	1,4080 (20)	14
27.	phenyl	1-chloro-3-phenyl-propanol-3	130—2	(8)	—	—	52
28.	phenyl	1-chloro-3-phenyl-propanol-3	75	(0,03)	—	1,5412 (20)	15
29.	phenyl	1-chloro-3-phenyl-3-acetoxypropane	84—5	(0,1)	—	1,5121 (20)	15
			52	(0,5)	—		
30.	phenyl	2-phenyloxetane	87—8	(8)	1,023 <sup>20</sup>	1,5288 (20)	15

Table IV.  
Physical properties of

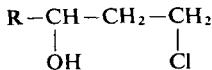
No	R	Formula	Molecular weight	Boiling point C° (Hg mm)	d <sub>4</sub> <sup>20</sup> gr/cm <sup>3</sup>
1.	methyl	C <sub>4</sub> H <sub>9</sub> ClO	108,57	67— 8 (20)	1,069
2.	ethyl	C <sub>5</sub> H <sub>11</sub> ClO	122,60	75— 6 (15)	1,044
3.	<i>n</i> -propyl	C <sub>6</sub> H <sub>13</sub> ClO	136,62	81— 2 (10)	1,012
4.	<i>i</i> -propyl	C <sub>6</sub> H <sub>13</sub> ClO	136,62	72— 3 (10)	1,020
5.	<i>n</i> -butyl	C <sub>7</sub> H <sub>15</sub> ClO	150,64	100— 2 (3)	0,997
6.	<i>t</i> -butyl	C <sub>7</sub> H <sub>15</sub> ClO	150,64	90— 2 (3)	1,005
7.	<i>c</i> -hexyl	C <sub>9</sub> H <sub>17</sub> ClO	176,68	138—40 (10)	1,075
8.	phenyl	C <sub>9</sub> H <sub>11</sub> ClO	170,50	125— 6 (6)	1,155
9.	benzyl	C <sub>10</sub> H <sub>13</sub> ClO	184,52	140— 2 (2)	1,137

Table V.  
Physical properties of

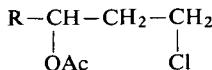
No	R	Formula	Molecular weight	Boiling point C° (Hg mm)	d <sub>4</sub> <sup>20</sup> gr/cm <sup>3</sup>
1.	methyl	C <sub>6</sub> H <sub>11</sub> ClO <sub>2</sub>	150,60	98—100 (35)	1,058
2.	ethyl	C <sub>7</sub> H <sub>13</sub> ClO <sub>2</sub>	164,64	75— 6 (9)	1,037
3.	<i>n</i> -propyl	C <sub>8</sub> H <sub>15</sub> ClO <sub>2</sub>	178,66	89— 90 (9)	1,019
4.	<i>i</i> -propyl	C <sub>8</sub> H <sub>15</sub> ClO <sub>2</sub>	178,66	83— 4 (3)	1,026
5.	<i>n</i> -butyl	C <sub>9</sub> H <sub>17</sub> ClO <sub>2</sub>	192,68	82— 4 (1)	1,002
6.	<i>t</i> -butyl	C <sub>9</sub> H <sub>17</sub> ClO <sub>2</sub>	192,68	76— 80 (1)	1,014
7.	<i>c</i> -hexyl	C <sub>11</sub> H <sub>19</sub> ClO <sub>2</sub>	218,72	125— 6 (2,5)	1,071
8.	phenyl	C <sub>11</sub> H <sub>13</sub> ClO <sub>2</sub>	212,54	136— 7 (2)	1,143
9.	benzyl	C <sub>12</sub> H <sub>15</sub> ClO <sub>2</sub>	226,56	124— 8 (2)	1,141

Table VI.  
Physical properties of

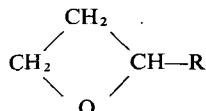
No	R	Formula	Molecular weight	Boiling point C° (Hg mm)	d <sub>4</sub> <sup>20</sup> gr/cm <sup>3</sup>
1.	methyl	C <sub>4</sub> H <sub>8</sub> O	72,10	59—60 (750)	0,847
2.	ethyl	C <sub>5</sub> H <sub>10</sub> O	86,13	87— 8 (748)	0,844
3.	<i>n</i> -propyl	C <sub>6</sub> H <sub>12</sub> O	100,16	110— 1 (753)	0,842
4.	<i>i</i> -propyl	C <sub>6</sub> H <sub>12</sub> O	100,16	102— 3 (753)	0,832
5.	<i>n</i> -butyl	C <sub>7</sub> H <sub>14</sub> O	114,18	141— 2 (753)	0,845
6.	<i>t</i> -butyl	C <sub>7</sub> H <sub>14</sub> O	114,18	132— 3 (742)	0,837
7.	<i>c</i> -hexyl	C <sub>9</sub> H <sub>16</sub> O	140,22	67— 9 (10)	0,936
8.	phenyl	C <sub>9</sub> H <sub>10</sub> O	134,17	76— 7 (4)	1,041
9.	benzyl	C <sub>10</sub> H <sub>12</sub> O	148,19	72— 4 (10)	1,063



$n_D^{20}$	$R_{MD}$		C %		H %		Cl %	
	found	calc.	found	calc.	found	calc.	found	calc.
1,4438	26,98	27,06	44,49	44,20	8,31	8,35	32,67	32,66
1,4478	31,43	31,68	48,75	49,0	8,91	9,05	28,78	28,92
1,4487	36,20	36,30	52,68	52,74	9,66	9,58	26,00	25,96
1,4520	36,12	36,30	52,65	52,74	9,63	9,58	26,06	25,96
1,4533	40,86	40,92	55,82	55,81	9,85	10,04	23,20	23,54
1,4563	40,77	40,92	55,72	55,81	9,90	10,04	23,24	23,54
1,4890	47,43	47,95	61,50	61,20	9,84	9,68	19,82	20,00
1,5402	46,35	46,50	63,17	63,35	6,46	6,49	20,74	20,78
1,5406	50,98	51,15	65,10	65,12	6,84	7,08	18,84	19,25



$n_D^{20}$	$R_{MD}$		C %		H %		Cl %	
	found	calc.	found	calc.	found	calc.	found	calc.
1,4278	36,58	36,53	48,03	47,85	7,53	7,36	23,54	23,54
1,4318	41,16	41,18	50,94	51,20	7,90	7,95	21,13	21,60
1,4352	45,78	45,83	53,82	53,79	8,39	8,46	19,70	19,85
1,4403	45,94	45,83	53,87	53,79	8,38	8,46	19,66	19,85
1,4390	50,56	50,48	55,95	56,20	8,80	8,89	18,25	18,41
1,4452	50,61	50,48	56,14	56,20	8,71	8,89	18,33	18,41
1,4720	57,19	57,56	60,70	60,41	8,95	8,75	16,10	16,18
1,5124	55,81	56,02	62,04	62,12	6,24	6,16	16,86	16,68
1,5218	60,53	60,67	63,43	63,60	6,60	6,67	15,21	15,65



$n_D^{20}$	$R_{MD}$		C %		H %		
	found	calc.	found	calc.	found	calc.	
1,3909	20,21	20,11	—	—	66,60	—	11,20
1,4028	24,90	24,73	68,46	69,77	11,34	11,63	
1,4110	29,54	29,35	70,87	71,96	12,00	12,06	
1,4066	29,61	29,35	71,35	71,96	11,94	12,06	
1,4195	34,15	33,97	72,95	73,63	12,24	12,38	
1,4157	34,21	33,97	73,18	73,63	12,30	12,38	
1,4644	41,31	41,01	76,66	77,08	11,59	11,50	
1,5296	40,04	39,87	80,21	80,51	7,40	7,46	
1,5540	44,68	44,52	80,74	81,02	8,08	8,16	

chloride for about 10–10 minutes. After precipitation the solution is carefully filtered through cotton into a bottle formerly cooled below  $-10^{\circ}\text{C}$  (-or into a dropping funnel belonging to a beforehand constructed apparatus, containing the GRIGNARD reagent). The solution thus obtained was used direct for the Grignard reaction without isolation.

4-chloro-2-butanol-2 was prepared after the reduction of chloro-ketone by lithium aluminum hydride [12]. 300 g (76%) of chlorocarbinol was obtained from 386 g 4-chloro-2-butanol. The synthesis of the compound from  $\beta$ -chloropropionaldehyde with magnesium iodide was also carried out in the following manner. Etheric solution of  $\beta$ -chloropropionaldehyde, prepared from 3 mole acrolein, was added dropwise from a double-walled dropping funnel (-in order to avoid trimerisation of  $\beta$ -chloropropionaldehyde, the temperature was maintained below  $-10^{\circ}\text{C}$  by means of ice-NaCl cooling between the two walls) to the absolute etheric solution of the GRIGNARD reagent prepared from 3 mole of magnesium (73 g) 3 mole of methyl iodide (426 g) and 1400 ml abs. ether, so that during the addition (2–3 hours) the temperature did not rise above  $0^{\circ}\text{C}$ , and then the mixture was stirred for an hour at room temperature. Following this the addition product was decomposed with aqueous acetic acid solution of somewhat larger amount than calculated (200 g acetic acid/100 ml water), under cooling. The aqueous phase was extracted with ether, and the combined etheric extractions were washed with sodium carbonate solution, dried over heated sodium carbonate and distilled. 100 g (31%) 4-chloro-2-butanol was obtained from 168 g (3 mole) acrolein.

4-chloro-2-butylacetate. The acetylation of chlorocarbinol can be performed with acetyl chloride in the presence of pyridine, or in a simpler way but with worse yield, with acetic anhydride. Both methods were applied for the preparation of 4-chloro-2-butylacetate. The acetylation with acetyl chloride has been published (12). Acetylation with acetic anhydride was carried out as follows: a few drops of concentrated sulphuric acid and then 1.45 mole of acetic anhydride were added to 1,2 mole of chlorocarbinol during 30 minutes, under constant stirring. The reaction is exothermic. Then the mixture was refluxed during 1,5 hours in an oil bath and the excess anhydride carefully decomposed with some water. The organic layer was separated from the aqueous one, washed with water and aqueous sodium carbonate solution. The combined and neutralized phases were extracted with ether. The organic phases were also combined, dried over anhydrous sodium carbonate and fractionated. 140 g of 4-chloro-2-butylacetate was obtained from 180 g of 4-chloro-2-butanol. Yield: 80%.

2-methyloxetane. A 2 litre three-necked bottle was equipped with a strong stirrer, thermometer, dropping funnel and a 40 cm VIGREUX column. The column was connected with a well-cooled descending cooler. 500 g of chloroacetate mixture was added dropwise to the mixture of 600 g of potassiumhydroxide, 600 g of sodiumhydroxide and 60 ml water, with vigorous stirring, at  $140^{\circ}\text{C}$  during a period of about two-three hours. In such an addition the rate of distillation is about 1 drop/sec. The bottle was heated in an oil bath so that oil reached the neck of the bottle. After introduction the temperature of the oil bath was raised to  $160^{\circ}\text{C}$  and kept there for an hour. The crude product was dried with potassiumhydroxide and fractionally distilled from metallic sodium. Yield.: 120 g (50%).

Chlorohydrines enlisted in Table IV, chloroacetates in Table V and oxetanes in Table VI were prepared starting from 3-3 mole acrolein, according to the method

described at 2-methyloxetane. The corresponding Grignard reagents were prepared from ethyl bromide, n-propyl bromide, i-propyl bromide, n-butyl bromide, t-butyl chloride, c-hexyl chloride, bromobenzene and benzyl chloride, according to the descriptions in Organic Syntheses. Acetylation was in every case carried out with acetic anhydride.

*β-chloropropiophenon* was prepared starting from 2 mole benzoylchloride by MATSUMOTO's method [45].

*1-phenyl-3-chloro-propanol-1* was prepared by the reduction of the former with lithium aluminum hydride by the method used for the reduction of *β*-chloroethylketone.

Mole refractions were calculated applying VOGEL's data [50].

\* \* \*

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### ИЗУЧЕНИЕ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ ДИОЛОВ И ОРГАНИЧЕСКИХ ОКИСЕЙ. IV

#### ПРИГОТОВЛЕНИЕ 2-ОДНОЗАМЕЩЕННЫХ ПРОИЗВОДНЫХ ОКИСИ ТРИМЕТИЛЕНА

М. Барток и А. Ш. Гильде

Авторы дают обзор о методах синтеза 2-однозамещенных четырехчленных органических окисей. Они приготовили 2-метил-, 2-этил-, 2-и-пропил-, 2-фенил- и в последнее время 2-н-бутил-, 2-т-бутил-, 2-ц-гексил- и 2-бензил- $\beta$ -окиси. Авторы высказывают, что эти циклические эфиры могут быть приготовлены сравнительно хорошим выходом (общее 70%) из хлороацетатов содержащих соответствующий первичный хлор.