

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

## Introduction. Preparation and Structure of Trimethylene Oxide

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The authors wish to deal in the future with the syntheses and study of chemical changes of cyclic ethers. As an introduction to the first part of this series, a short summary of their aims and tasks is given. They deal with the synthesis of trimethylene oxide, the basic compound of four-membered cyclic ethers, as well as with the development and the present state of researches of its structure.

### 1. Introduction

Cyclic compounds form a very significant part of organic chemistry. These compounds became the subject of meaningful studies because of their frequency in the nature, widespread application in the practice and of the continuous widening of the circle of their utilisation. All this made important to take efforts to clear up several questions of theoretical importance. Cyclic systems and their chemical conversions are extensively treated in a number of publications. However, our knowledge is far not complete especially with regard to the revealing of relative regularities of cyclic compounds with different members. The present investigation includes heterocyclic compounds containing one oxygen atom, i. e. the syntheses and study of chemical transformations of cyclic ethers.

This work deals with questions concerning the preparation and structure of trimethylene oxide (1,3-epoxide, in English literature oxetane, in Russian  $\beta$ -oxide). First, as an introduction we give a short summary of the tasks before us and the aims of our researches.

The theoretical importance of four-membered cyclic ethers has been emphasized in numerous publications dealing with their preparation, physical and chemical properties. However, the chemistry of oxetanes was dealt with in detail only during the last decade. At the beginning of these investigations the chemistry of three-, five- and six-membered cyclic ethers, as compared to four membered ones, was largely known. Important studies within the circle of this group of compounds, however, are in progress even in these days since introduction and application of new methods and measuring apparatuses opened new vistas here, too. Thus it became possible to throw away old and faulty points of view and theories, to put in order the frequently discussed problems and the obtained data could be made more accurate, applicable for relative evaluations. To make clear the theoretical problems in the chemistry of these compounds is of major importance, thereby the practice gains considerable help. The practical application of 1,2-epoxides, of furan and

its hydrated derivatives as well as of various pyran derivatives themselves or as starting chemicals is widely known for organic chemists.

The preparation and study of chemical reactions of four-membered cyclic ethers got far less emphasis. This view is illustrated in ELDERFIELD'S [1] monography in 1950, which treats 1,2-epoxides on forty pages while oxetanes on one. The backwardness of researches in this field has several reasons. As a rule, four-membered cyclic systems are less frequent in nature as compared to other cyclic compounds. Four membered rings are also found in the nature as *e. g.* cyclobutane skeleton which appears in pynane serie of terpenes, in penicillin antibiotics  $\beta$ -lactam ring and oxetane skeleton is supposed to be in trichothecin [2] and terrein [3]. Five- and six-membered rings are considerably more numerous. KNUNJANTS and his coworkers [4] have summarized the problem of frequency, spreading and formation of four-membered cycles. Some of their statements could not be accepted.

The synthesis of trimethylene oxide and its derivatives is not acceptable for industrial purposes because of the low yield. Thus industry could not request four-membered cyclic ethers. 1,2-epoxides, five- and six-membered cyclic ethers were easy to obtain from olefines and furfurol, respectively. Application in industry and everyday life of all these cyclic ethers is well known.

Recently the interest in investigations of trimethylene oxide and its derivatives has arisen. Efforts to study this subject have earlier been taken but were not continued. *E. g.* in 1916 DERICK and BISSELL [5] turned to four-membered cyclic ethers but the first paper of the series remained uncontinued. In 1954 GAYLORD and his coworkers started a series on the same subject [6] but here the progress was broken, too. The behaviour of this group of compounds underwent a thorough and long study in 1950 by SEARLES and his coworkers, and their results in the study of oxetanes have been published in subsequent papers from this time on. Their investigations endeavoured to fill the abyss in the line of cyclic ethers and their significant results made possible to compare the physical and chemical behaviour of the members of series of cyclic ethers. As long as our knowledge of one member of the series is not complete, to establish general rules is not possible.

In view of this it is reasonable that the necessity to study oxetanes sooner or later had to arise on organic chemistry.

Investigations so far done claimed that in respect of geometry, stereochemistry and chemical changes of four-membered cyclic ethers, they from an independent system within cyclic ethers, that is, regarding their specificity they could not fit in any other family of compounds.

The Institute of Organic Chemistry of this University got into closer connection with the study of trimethylene oxide and its chemistry in 1954 [7]. Later the problems arisen led to the widening of the theme and resulted in a systematic study, starting from the preparation of simple oxetanes through the synthesis of more complicated four-membered cyclic ethers, of their chemical transformations. We had a double aim before us:

*a)* to study the theoretical problems of four-membered cyclic ethers in order to establish the relative connections between their chemical transformations. Thus the mechanism of formation of oxetanes formed from 1,3-halohydrins and their acetates has been examined. In order to establish the stability of cyclic ethers, their thermochemistry, thermal decomposition and chemical changes in presence of different contact catalysts (isomerisation, hydrogenation, hydratation and dehydra-

tation, etc.) have been also examined. By the study of catalytic changes of cyclic ethers with different number of members it becomes possible not only to examine the relative stability of certain members of the series but also to determine the direction of different cleavage reactions depending upon experimental conditions. This way we gain some data concerning the activity and selectivity of the catalysts, what is an addition to the knowledge of the mechanism of catalysts.

b) on the other hand we attempt to make possible the application in practice of four-membered cyclic ethers by studying their syntheses and their chemical changes. Considerable results have been attained in this respect by FARTHING [8], [9], CAMPBELL [10], [11] and by ROSE and his coworkers [12]. They all investigated the application of oxetanes in the field of plastics.

The practical use of trimethylene oxide and its derivatives can be realized only in cheap and large-scale syntheses. Therefore it is necessary to develop more precisely a method [13], which prepares oxetanes by the gas phase oxidation of saturated hydrocarbons in presence of corresponding catalysts.

## 2. Preparation of trimethylene oxide

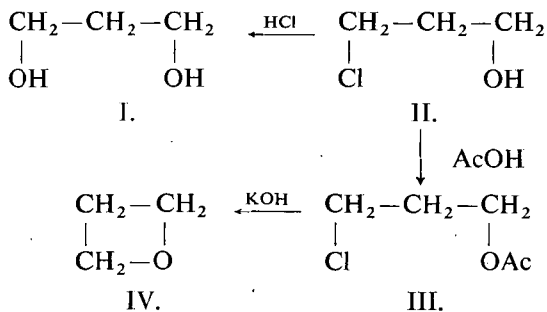
Methods of preparation of four-membered cyclic ethers can be divided into two groups:

a) Synthesis starting from 1,3-disubstituted compounds. Diols, halohydrins, haloacetates, aminoalcohols, mono- and ditosylates and brosilates, resp., of 1,3-diols and cyclic carbonates of 1,3-diols all serve as starting materials of this synthesis.

The best method in this group is WILLIAMSON's intramolecular ether synthesis starting from 1,3-halohydrins and haloacetates, respectively.

b) Oxetane molecule is built up from two units by means of the interaction of olefine and oxocompound, by photocatalysis. This method is not completely worked out thus is not so frequent, although it seems very simple. With its application it becomes possible to prepare oxetanes with more complicated structure from compounds easy to obtain.

A very good method to prepare trimethylene oxide is the intramolecular ring-closure starting from trimethylene glycol, through halohydrin. The first synthesis of trimethylene oxide, the basic compound of four membered cyclic ethers was reported by REBOUL [14]. He obtained trimethylene oxide from trimethylene chlorohydrin with potassium hydroxide with 5% yield. The most important physical constants of trimethylene oxide were determined by IPATIEV [15] who prepared it with the same method. All the other methods with one or two exceptions start from 3-chloropropyl acetate. A general scheme of the synthesis can be given as follows:



Starting from chloroacetate, oxetanes are obtained with better yield than from chlorohydrin. The reason of this and the mechanism of formation was given by DITTMER and his coworkers [16].

The detailed study of the mechanism of chemical reactions resulting in cyclic ethers from 1,3-halohydrins and haloacetates will be given in our future publications.

The description of a method starting from 3-chloropropylacetate is given by DERICK and BISSELL [5], who received trimethylene oxide with a yield of 22,5%.

All other methods applying 3-chloropropylacetate [17, 18, 19, 41, 20, 21, 36, 22, 39, 40, 12, 16, 57, 23, 38, 24] modify only slightly DERICK and BISSELL's method, or follow it completely. More significant differences could be found only in the preparation of starting substances II and III. The preparation of trimethylene chlorohydrin in greater amount for laboratory purposes can be best effected by MARVEL and CALVERY's method [25], according to which it is prepared from 1,3-propanediol and hydrogen chloride in a continuous system. According to LESPIEAU [19] and ALLEN and SPENGLER [26] II. can be converted into III by glacial acetic acid. BERMEJO and ARANDA [18] prepared 3-chloropropylacetate from 1,3-dichloropropane with silver acetate, while HENRY [27, 28] and more recently SEARLES [22] from trimethylene chlorobromide with potassium acetate in acetic acid medium. A simple method to prepare 3-chloropropyl acetate in less amount is described by BENNETT and HEATHCOAT [29]. 3-chloropropylacetate can be obtained in one step from 1,3-propanediol with acetyl chloride. This possibility was first dealt with by BOGERT and SLOCUM [30]. With a slight modification of their method ROSE [12] prepared 3-chloropropylacetate with 65% yield. Trimethylene oxide is formed from 3-chloropropylacetate by ring closure in the presence of bases. Mostly sodium and potassium hydroxides are used as bases. The attained maximum yield is 40–45%.

ALLEN and HIBBERT [31] prepared trimethylene oxide from 3-bromopropylacetate, synthesized from trimethylene glycol with acetyl bromide. IV was prepared direct from trimethylene glycol by SCHMOYER and CASE [32] with a yield lower than the chloroacetate method. The procedure involves dropping of concentrated sulphuric acid solution of glycol to hot aqueous solution of sodium hydroxide. Trimethylene oxide is distilled from the mixture.

To prepare trimethylene oxide was attempted in other ways, too, but all these attempts failed to result in cyclic ether. *E. g.* by the catalytic pyrolysis of cyclic carbonate of 1,3-propanediol, allyl alcohol was obtained with a yield of 59%, however, formation of IV was not observed [33]. The dehydration of trimethylene glycol on  $\gamma$ -aluminum oxide catalyst resulted in trimethylene oxide neither [34]. In this case propionaldehyde, allyl alcohol, propyl alcohol, ditrimethylene glycol and  $\alpha$ -methyl- $\beta$ -ethylacrolein were obtained as a result of the conversion.

We think it necessary to note that simultaneously with ring-closing reactions, different by-reactions also take place. This is to be seen from data of Table I. The main reaction is mostly accompanied by formation of allyl alcohol, which is formed by the nucleophilic elimination of hydrogen chloride. Intermolecular nucleophilic substitution also plays part [SN<sub>2</sub>] to a less extent, as well as the cleavage of the molecule into two, as a result of which ethylene and formaldehyde are formed. Formaldehyde undergoes secondary reactions.

It is also worthy to note that CHAN and his coworkers [24] have prepared 3-deutero-, 2, 2, 4, 4-tetradeutero- and O<sup>18</sup>-trimethylene oxides. Physical constants of the three compounds were not published.

Table I summarizes the physical constants and yield of trimethylene oxide, as determined by different authors.

Table I

No.	Year of publication of syntheses	Starting compound	Applied bases	Yield in %	Trimethylene oxide			References
					boiling point C° (Hg mm)	d gr/cm <sup>3</sup>	n <sub>D</sub> <sup>20</sup>	
1	1878	trimethylene chlorohydrin	KOH	5	50°	—	—	14
2	1914	trimethylene chlorohydrin	KOH	—	45–46 (736)	0,8757 <sup>24</sup>	1,3901 <sup>18,5</sup>	15
3	1916	3-chloropropyl acetate	KOH	22,5	47,8 (760)	0,8930 <sup>25</sup>	1,3897 <sup>25</sup>	5
4	1926	3-chloropropyl acetate	KOH	32–3	45,8–46,4 (760)	—	—	17
5	1929	3-chloropropyl acetate	KOH	—	48–50	—	—	18
6	1934	3-bromopropyl acetate	KOH	21	45,5–47,5	0,8930 <sup>24</sup>	1,3895 <sup>25</sup>	31
7	1940	3-chloropropyl acetate	KOH	—	48,2 (761)	0,9038 <sup>18</sup>	1,392 <sup>18</sup>	19
8	1940	3-chloropropyl acetate	KOH	—	47,7 (760)	—	1,3928 <sup>18,5</sup>	41
9	1949	3-chloropropyl acetate	KOH	42–44	47–48	—	1,3905 <sup>26</sup>	20
10	1951	3-chloropropyl acetate	KOH + NaOH	42–45	48 (750)	—	1,3895 <sup>25</sup>	21
11	1953	—	—	—	45,7–46,5 (741)	0,9001 <sup>20</sup>	1,3915 <sup>20</sup>	35
12	1953	3-chloropropyl acetate	KOH + NaOH	—	47 (750)	—	1,3893 <sup>25</sup>	36
13	1954	3-chloropropyl acetate	KOH + NaOH	39–49	47 (745)	—	—	22
14	1955	3-chloropropyl acetate	KOH	—	—	—	1,3905 <sup>23</sup>	39
15	1955	3-chloropropyl acetate	KOH	40	—	—	1,3940 <sup>20,5</sup>	40
16	1956	3-chloropropyl acetate	KOH + NaOH	—	48 (770)	—	1,3929 <sup>20</sup>	12
17	1957	3-chloropropyl chloracetate	KOH	24,3	46–48	—	1,3885 <sup>26</sup>	16
18	1957	3-chloropropyl trimethylsilyl ether	KOH	41	47–49	—	1,3910 <sup>23</sup>	16
19	1957	3-chloropropyl acetate	KOH	—	47	—	1,3868 <sup>25</sup>	57
20	1958	3-chloropropyl acetate	KOH	24	47,0–47,2	—	1,3920 <sup>25</sup>	23
21	1959	3-chloropropyl acetate	KOH + NaOH	—	—	—	1,3899 <sup>25</sup>	38
22	1959	trimethylene glycol	NaOH	~ 30	—	—	—	32
23	1960	3-chloropropyl acetate	NaOH + KOH	—	48,5	—	1,3898 <sup>25</sup>	24

In the course of our researches we have also dealt with the synthesis of trimethylene oxide by different methods. Under laboratory conditions the easiest and most profitable method is the ring closure in presence of bases, starting from trimethylene glycol through 3-chloropropylacetate. This latter was prepared by MELTZER and KING's method [37]. The essence of the method is that butanediol is treated in presence of anhydrous calcium chloride with acetylchloride, applying strong cooling, thereupon 3-chlorobutylacetate was attained in one step. On applying this method to 1,3-propanediol, 3-chloropropylacetate was prepared with 67% yield. From this latter trimethylene oxide was received on effect of potassium hydroxide by the method described in Experimental, in 42–45% yield.

*On the structure and main physical constants of trimethylene oxide*

Investigations on the structure of trimethylene oxide are in progress even at the present time. Introduction of new physical and physico-chemical methods and their widespread application brought something new in the study of structure of organic compounds, and this brings us closer to the knowledge of the real structure of the compound in question.

Applying BAYER's theory (1885) developed for on the structure of homocyclic compounds, on the basis of plane geometry (in some respect denied today) to the four-membered trimethylene oxide ring, the basic compound of four-membered cyclic ethers would be a stretched, planar square molecule. However, examination of the geometry of the ring brought different results. According to the modern conception, trimethylene oxide molecule can be regarded as planar, however, the valency angle differs from  $90^\circ$ .

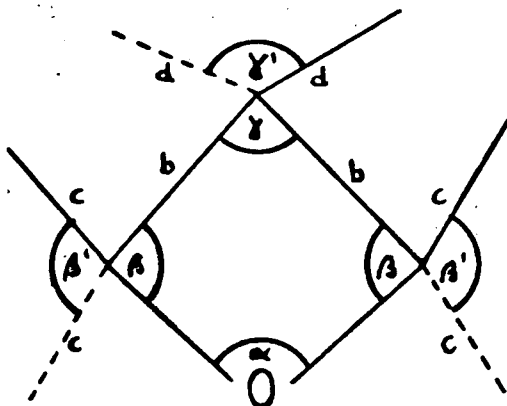
Some of the statements of the Introduction of this paper is also characteristic of the development of the research work regarding the structure of trimethylene oxide. After its discovery (REBOUL, 1878) nothing had happened for thirty years in the study of structure of four-membered cyclic ethers. The main physical constants of trimethylene oxide (boiling point, density, refractivity) were determined by IPATIEV [15] only in 1914. Its dipole moment was determined by HIBBERT and ALLEN [43] in 1932 (2,01 D), and the valency angle of the oxygen atom was found as  $102^\circ$ . This is an important date, for it was the starting point of studies on the structure of trimethylene oxide. Erroneous data were corrected in 1934 [31] and the C—O—C valency angle, calculated from experimental data, was given as  $94^\circ$ . In the same work the C—C and C—O bond distances as well as the dipole moments were also given. This latter value is reported in a table summarizing dipole moments published in 1934 [44]. According to more recent and more exact studies, the dipole moment of trimethylene oxide is  $1,93 \pm 0,01$  D [57, 58, 55, 24]. In a paper published in 1940 DE VRIES ROBLES [45] gives the results of stereostructural calculations of cyclic compounds. The most probable state of the trimethylene oxide molecule was determined on the principle of minimum energy. The stretching energy was calculated using PAULING's data, and its minimum was found when the molecule had a planar conformation. Stereochemical models also brought the same results. Further investigations [46, 47] all endeavour to give a deeper insight in the structure of trimethylene oxide.

A considerable progress in this field was the application of electron diffraction,

Raman, — infrared and microwave — spectroscopy. The Raman spectrum of trimethylene oxide was first taken by KOHLRAUSCH and REITZ [41] and the infrared spectrum by BARROW and SEARLES [36]. The importance of this problem is supported by the fact that a number of groups of researchers have concerned themselves with the infrared spectra [48, 49] and their analysis [40, 50, 51]. From the Raman and infrared spectra of trimethylene oxide ZÜRCHER and GÜNTHARD [40] have stated the normal vibration of the ring and from this deductions on the thermodynamical properties of trimethylene oxide were done. In their calculation data regarding the geometry of the ring were taken into account (SHAND's electron diffraction data) and on the basis of the results the ring was regarded as a planar one. However, they noticed that slight differences from the plane could not be estimated by the method of electron diffraction. In a later publication [52] applying Raman-, polarisation- and microwave-spectroscopy, some more exact data on the thermodynamical properties of trimethylene oxide were given.

The application of microwave spectroscopy in the study of the structure of trimethylene oxide was introduced on a larger scale by GWINN and his coworkers [53, 24, 54]. The microwave spectra of trimethylene oxide and deuterized trimethylene oxides were obtained. These investigations aimed to give a more exact picture of the planar and spatial character, resp. of the ring. According to the classical strain theory, trimethylene oxide ring is planar. On the contrary, hydrogen atoms favor the spatial arrangement of the ring. The real state is determined by the resultant of the opposing forces. GWINN and his coworkers, using microwave spectroscopy, calimed, that trimethylene oxide is essentially a planar molecule. The four membered ring may be considered to be vibrating about the planar configuration in all the vibrational states. As a result of their investigations concerning the structure of trimethylene oxide the following bond distances and valence angles are given:

<i>a</i> .....	1,449 ± 0,002 Å°
<i>b</i> .....	1,549 ± 0,003 Å°
<i>c</i> .....	1,091 ± 0,002 Å°
<i>d</i> .....	1,100 ± 0,003 Å°
$\alpha$ .....	91°59' ± 7'
$\beta$ .....	91°44' ± 3'
$\gamma$ .....	84°33' ± 1'
$\beta'$ .....	110°18' ± 10'
$\gamma'$ .....	110°44' ± 3'



Some physical constants of trimethylene oxide found in the literature and determined by us are given below:

Formula .....	$C_3H_6O$	O .....	27,55 %
Molecular weight .....	58,078	Boiling point (760 Hg mm): .....	48°
C .....	62,04 %	Density ( $d_4^{20}$ ) .....	0,8963 gr/cm <sup>3</sup>
H .....	10,41 %	Refractivity ( $n_D^{20}$ ) .....	1,3936

Mole refraction ( $R_{MD}$ )		
Calculated .....	15,89	56
Found .....	15,47	
Difference .....	0,58	
Dipole moment .....	$1,93 \pm 0,01$ D	24
Specific heat ( $C_p^0$ ) (at 25,1°C) .....	14,20 cal/degree mole	40
Entropy ( $S^0$ ) (at 25,1°C) .....	63,399 cal/degree mole	40
Characteristic absorption band of the infrared spectrum:	10,15 $\mu$	48
Characteristic values of the Raman spectrum:		40,52

It must be noted that the following physical and physicochemical properties of trimethylene oxide could not be found in literature:

freezing point, viscosity, surface viscosity, magnetic susceptibility, critical temperature, evaporation heat, heats of combustion and formation.

### Experimental

*1-chloro-3-acetoxyp propane* was prepared by MELTZER and KING's method [37]. 206 g of powdered calciumchloride (1,89 mole) was added to 761 g of trimethylene glycol (10 mole) by constant stirring, the mixture was cooled with ice and NaCl to  $-10^\circ\text{C}$  and under continued stirring 955 g of acetyl chloride (12,15 mole) was added dropwise to the mixture in about three hours. The temperature had risen up to  $20^\circ\text{C}$ . The reaction mixture was then stirred for twenty hours at room temperature, refluxed for one hour cooled and poured into 1500 g of ice. The two layer thus obtained were separated, the aqueous one extracted with ether. The organic layer was combined with the unified extracts washed with 20% aqueous NaCl and 20% aqueous  $\text{Na}_2\text{CO}_3$  solutions and dried over anhydrous  $\text{MgSO}_4$ . Fractional distillation gave 913 g of 1-chloro-3-acetoxyp propane (yield: 67%).

Boiling point:  $68-70^\circ\text{C}$  (20 mm);  $d_4^{20}$ : 1,112;  $n_D^{20}$ : 1,4327;  $R_{MD}$ : found 31,90; calculated [56]; 31,88

Analysis: Calculated for  $\text{C}_5\text{H}_9\text{ClO}_2$

Found:	C: 43,97;	H: 6,64;	Cl: 25,96%.
	C: 44,02;	H: 6,61;	Cl: 25,84%.

*Trimethylene oxide* was prepared according to NOLLER [20] by ring closure (KOH). A 2 l three-necked bottle was equipped with stirrer, thermometer, dropping funnel and a 40 cm Vigreux colum. The column was connected with a efficient cooler (because of the low boiling point and the great tension of trimethylene oxide, the main source of failure is the insufficient cooling). In the flask to the vigorously stirred mixture of 672 g of KOH (12 mole) and 60 ml water, 546 g of 1-chloro-3-acetoxyp propane (4 mole) was added dropwise at  $140^\circ\text{C}$  so that the velocity of distillation should be about 1 drop/sec. The reaction was complete after about one hour. The bottle was heated in an oil bath so that oil reached the neck of the bottle. The temperature of the oil bath was then raised to  $150^\circ\text{C}$  and maintained there for an hour. The crude product was dried over KOH and distilled through a column with a theoretical plate number of 30. Yield: 100 g (43%).

Boiling point:  $48^\circ\text{C}$  (760 mm);  $d_4^{20}$ : 0,8963;  $n_D^{20}$ : 1,3936  
 $R_{MD}$ : found 15,47; calculated [56]: 15,89.

\* \* \*



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## ИЗУЧЕНИЕ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ ДИОЛОВ И ОРГАНИЧЕСКИХ ОКИСЕЙ. I

### ПРИГОТОВЛЕНИЕ И ПОСТРОЕНИЕ ОКИСИ ТРИМЕТИЛЕНА

М. Барток и И. Анйок

В будущем авторы намерены заниматься приготовлением и изучением химических превращений органических окисей. Как введение первой публикации этой серии, они дают краткий обзор их задач и целей научной работы. Они занимаются синтезом окиси триметилена и также изучают развитие и современное положение исследований структуры данного соединения.

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