39. Studies on the Conversions of Diols and Cyclic Ethers

Part 48[1])

Dehydration of Alcohols and Diols on the Action of Dimethylsulfoxide

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Summary

The transformations of 13 alcohols and 13 diols in the presence of a small amount dimethylsulfoxide ($^1\!/_{16}$ mol) were studied. Relationships were found between the type of the hydroxy compound and the selectivity of the transformation, and conclusions were drawn regarding the transformation mechanism. The ether formation observed with certain alcohols proceeds *via* a carbenium cation. The reaction conditions applied were found suitable for inducing water elimination from the ditertiary 1,2- and 1,3-diols (pinacol rearrangement, 1,2-elimination). From the 1,4- and 1,5-diols the corresponding oxacycloalkanes can be obtained in good yield. Cyclodehydration occurs by intramolecular nucleophilic substitution, *via* a concerted mechanism. The effect of DMSO is exerted directly, and proton-catalysis occurs simultaneously.

1. Introduction. - During the past twenty years a number of publications have appeared on the transformations of diols on the action of dimethylsulfoxide (DMSO) (see, for example, review [2]). The transformations of 1,2- and 1,3-diols lead not only to the formation of dienes, oxo compounds and unsaturated alcohols [3], but in certain cases to dioxacycloalkanes [4] [5]. For the higher diol homologues the main reaction is cyclodehydration to the cyclic ether [3] [6-10], generally with good yield, but side-reactions (diene formation) sometimes accompany this process. It is a common feature of these investigations that the reagent was used in large excess, the diol: DMSO ratio usually lying in the range 1:4-1:19.

It has recently been demonstrated in the transformations of various benzyl alcohols [11] that at very high alcohol: DMSO ratios (16:1) the olefin formation and certain oxidation reactions to be observed when the reagent is in high excess over the alcohol can be totally suppressed, and ethers can be obtained in excellent yields.

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Table 1. *Transformations of alcohols in presence of DMSO*

Starting alcohol	Reaction conditions			Conversion [%]	Product distribution [mol %]	
	Method, temp.[°C]	Time [h]	Alcohol: DMSO ratio			
1-Butanol	A, 195	24	10:1	0	-	
2-Butanol	A, 195	24	5:1	0	-	
t-Butyl alcohol	A, 195	24	114:1	20	2-Methylpropene	100
	A, 195	3	16:1	100	2-Methylpropene	100
Cyclohexanol	A, 195	24	5:1	2	Cyclohexene	100
	C, 175	24	16:1	20	Cyclohexene	60
					Dicyclohexyl ether	40
1-Cyclohexyl-ethanol	C, 175	24	16:1	14	Ethylidene cyclohexane	88
					Vinylcyclohexane	12
Benzyl alcohol	A, 175	10	16:1	85	Dibenzyl ether	100
	C, 175	10	16:1	100	Dibenzyl ether	100
1-Phenyl-ethanol	C, 175	5	16:1	100	Styrene	13
					Bis(*α*-methylbenzyl) ether	80
					Unidentified	3+4
1-Phenyl-propanol	C, 175	2.5	16:1	75	1-Phenyl-propene	40
					Bis(*α*-ethylbenzyl) ether	60
2-Phenyl-ethanol	C, 175	24	16:1	0	-	
1-Phenyl-2-propanol	C, 195	6	16:1	60	1-Phenyl-propene	51
					Unidentified	30+19
Allyl alcohol	A, 175	24	16:1	9	Diallyl ether	100
3-Phenyl-2-propene-1-ol	C, 175	3	16:1	100	Bis(3-phenyl-2-propenyl) ether	100
2-Cyclohexene-1-ol	C, 175	2	16:1	100	1,3-Cyclohexadiene	40
					Bis(2-cyclohexenyl) ether	60

In our work we have employed similar reaction conditions (high reactant: DMSO ratios) with the aims of (i) examining whether the above literature findings [11] can be extended to other compounds not of benzyl alcohol type, (ii) establishing the reaction pathways of various diols under such reaction conditions and comparing these with the results obtained in the presence of a large reagent excess, and (iii) discovering the mechanisms of the transformations, *i.e.* the formation of ethers from the alcohols, and of cyclic ethers from the diols, and comparing the mechanism found to hold for cyclodehydration with the mechanism assumed for the process occurring with a high reagent excess.

The experimental results are given in the *Tables 1-5.*

2. Results and discussion.

- 2.1. *Dehydration of alcohols.* Examinations with aliphatic alcohols and cyclohexanol *(Table 1)* indicate that the primary and secondary alcohols do not undergo, or undergo only very slight reaction at an alcohol: DMSO mole ratio of 16:1. At the same time, *t*-butyl alcohol very readily undergoes intramolecular water elimination. This reaction still occurs at an extremely high alcohol excess, ether formation not being observed.

Emert et al. [11] delt with the transformations of 1-phenyl-ethanol, and additionally only various ring-substituted benzyl alcohols. We employed the reaction conditions they had used, and studied some other compounds of *type* **1**, primarily

Table 2. *Transformations of 1,2- and 1,3-diols in presence of DMSO*

Starting diol	Reaction conditions			Conversion [%]	Product distribution [mol %]	
	Method, temp. [°C]	Time [h]	Diol: DMSO ratio			
2,3-Butanediol[a]	A, 195	24	16:1	29	Ethyl methyl ketone	53
					3-Buten-2-ol	21
					Unidentified	7+9+10
Pinacol	A, 195	18	16:1	100	2,3-Dimethyl-1,3-butadiene	11
					3,3-Dimethyl-2-butanone	64
					Unidentified	10+15
	B, 180-185	24	12:1	100	2,3-Dimethyl-1,3-butadiene	45
					3,3-Dimethyl-2-butanone	55
2,4-Pentanediol[a]	A, 195	24	8:1	40	Pentadienes	47
					3- and 4-Penten-2-ol	36
					Unidentified	17
	B, 180-190	16	8:1	55	Pentadienes	48
					3- and 4-Penten-2-ol	30
					Unidentified	14+6+2
2,4-Dimethyl-2,4-pentanediol	A, 185	16	16:1	100	2,4-Dimethylpentadienes	47
					2,4-Dimethyl-4-penten-2-ol	47
					Unidentified	6
	B, 180-190	10	16:1	100	2,4-Dimethylpentadienes	55
					2,4-Dimethyl-4-penten-2-ol	45

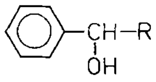
[a] Isomeric mixture.

Table 3. *Transformations of 1,4- and 1,5-diols in presence of DMSO*

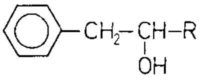
Starting diol	Reaction conditions			Conversion [%]	Product distribution [mol %]	
	Method, temp. [°C]	Time [h]	Diol: DMSO ratio			
1,4-Butanediol	A, 180	16	16:1	100	Tetrahydrofuran	100
1,5-Pentanediol	A, 195	12	16:1	100	Tetrahydropyran	100
1,6-Hexanediol	A, 195	24	3:1	55	Hexamethylene oxide	9
					2-Methyltetrahydropyran	1
					Resinous products	90
	B, 190-200	20	8:1	50	Hexamethylene oxide	10
					2-Methyltetrahydropyran	1
					Resinous products	89
1,4-Pentanediol	A, 195	24	10:1	100	2-Methyltetrahydrofuran	100
1,5-Hexanediol	A, 195	24	3:1	85	2-Methyltetrahydropyran	100
2,5-Hexanediol[a]	A, 195	16	16:1	100	2,5-Dimethyltetrahydrofuran[b]	95
					Unidentified	5
	B, 185-195	16	16:1	100	2,5-Dimethyltetrahydrofuran[b]	100
2,6-Heptanediol[a]	A, 200	6	10:1	100	2,6-Dimethyltetrahydropyran[c]	90
					Unidentified	10
2,5-Dimethyl-2,5-hexanediol	A, 180	16	16:1	100	2,2,5,5-Tetramethyltetrahydrofuran	82
					2,5-Dimethylhexadienes	18
2,6-Dimethyl-2,6-heptanediol	A, 180	18	16:1	100	2,2,6,6-Tetramethyltetrahydropyran	20
					Cyclogeraniolenes	2
					2,6-Dimethylheptadienes	78

[a] Isomeric mixture. [b] *cis/trans* = 55:45. [c] *cis/trans* = 70:30.

with the aim of establishing the influence of group R on inter- and intramolecular dehydration. The parent compound benzyl alcohol (R = H) is readily transformed to dibenzyl ether, but if R = alkyl, intramolecular water elimination occurs as well, to an extent depending on the effects of other stabilizing factors.



1 R=H, Me, Et



2 R= H, Me

With compounds of *type* **2**, *i.e.* not of benzyl alcohol type, ether formation is likewise not observed.

Analogous findings can be made for the transformations of some compounds of allyl alcohol type under the same conditions as above: allyl alcohol displays very low reactivity; cinnamic alcohol yields ether with 100% selectivity; and 2-cyclohexen-1-ol exhibits both reactions (inter- and intramolecular water elimination).

2.2. *Dehydration of diols.* From a comparison of the results relating to the diols in *Tables 2* and *3*, it may be seen that the disecondary 1,2- and 1,3-diols examined have lower reactivities than the 1,4- and 1,5-diols. The ditertiary compounds, however, undergo transformation with the same reactivity as the latter by means of rearrangement, *i.e.* pinacol leads to 3,3-dimethyl-2-butanone in good yield. The yield is much better than in the transformations in a large excess of DMSO [3], where, depending on the temperature, it is only 20–30%. 1,2-Elimination occurs in similar ease with 2,4-dimethyl-2,4-pentanediol, to give unsaturated alcohol and diene.

At a diol:DMSO ratio of 16:1, most open-chain 1,4- and 1,5-diols lose water and are converted to the corresponding cyclic ether. It may be observed that, as regards 1,4- and 1,5-diols with analogous structure, the latter always have lower reactivities: a longer reaction time, a higher temperature, and possibly a larger amount of reagent are necessary for attainment of the same conversion. This tendency can also be seen in the formation of the 7-membered ring in the case of the diprimary diols: for 1,6-hexanediol, complete conversion is not achieved even at a diol: DMSO ratio of 3:1.

This observation is in accordance with what has been reported [12] in the ring-closure reactions of other compounds (ω-haloalkylmalonic acid esters, chloroalcohols) taking place by nucleophilic substitution. The ring-closure rate varies with the number of ring atoms in these cases, in the following sequence: $4 < 5 > 6$.

In contrast with the product distribution observed in the case of a large excess of reagent, 2,5-dimethyl-2,5-hexanediol gives 2,2,5,5-tetramethyltetrahydrofuran in excellent yield, while at the same time the main process for the corresponding ditertiary 1,5-diol is diene formation. One of the cause of this phenomenon is the different reactivities of the cyclic ethers formed: under the reaction conditions of the formation, the 5-membered cyclic ether is much more stable than the 6-membered analogue *(Table 4).* We made a similar observation during

Table 4. *Reactions of α,α,ω,ω-tetrasubstituted cyclic ethers under transformation conditions of diols*

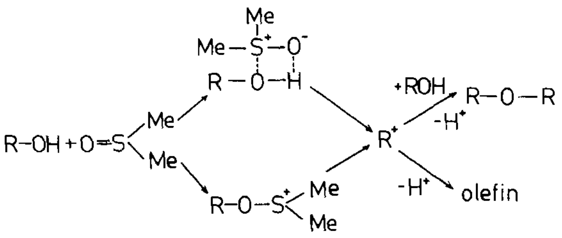
Starting cyclic ether	Reaction conditions[a]) Temp. [°C]	Time [h]	Conversion [%]	Product distribution [mol%]	
2,2,5,5-Tetramethyltetrahydrofuran	180	16	12	2,5-Dimethyl-1,5-hexadiene	42
				2,5-Dimethyl-2,4-hexadiene	58
	180	16[b])	50	2,5-Dimethyl-1,5-hexadiene	12
				2,5-Dimethyl-2,4-hexadiene	88
2,2,6,6-Tetramethyltetrahydropyran	180	16	100	2,6-Dimethyl-1,6-heptadiene	12
				2,6-Dimethyl-1,5-heptadiene	53
	180	16[b])	100	2,6-Dimethyl-2,6-heptadiene	12
				Cyclogeraniolenes	5
				Unidentified	3 + 15

[a]) Cyclic ether: DMSO mol ratio 16:1; method A.

[b]) The reaction mixture also contained 1 drop of water.

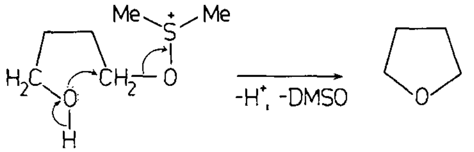
a study of the ring-closures of these two diols under heterogeneous catalytic conditions [13]. Another role in the resulting product distribution is played by the above-mentioned different ring-closure rates.

2.3. *Mechanism of transformation of alcohols.* That these processes take place *via* a carbenium cation is indicated by the literature data and by results of the present work: (i) the observation by *Emert et al.* [11] that the reaction of 1-phenylethanol occurs by racemization, and that a considerable proportion of the recovered alcohol is likewise racemized; (ii) the fact that ether formation proceeds only in the case of those compounds (allyl and benzyl alcohols) that display enhanced reactivities as regards cleavage of the C—O-bond; (iii) the observation that the ether formation is accompanied by olefin formation, which becomes the main reaction in certain cases. On this bases, in accordance with the literature references, the alcohols interact with the reagent to give a cyclic formation [8] or an alkoxysulfonium salt [11] [14]; in the case of alcohols with enhanced reactivities, these readily lead to stable (tertiary, allyl, benzyl) carbenium cations, which are stabilized by ether or olefin formation *(equ. 1)*. The data obtained suggest that the ratio of the two processes is influenced by steric and electronic factors.



(1)

2.4. *Mechanism of transformation of diols.* - 2.4.1. *Direct action of DMSO.* During the transformation of 1,4- and 1,5-diols, the interaction of one of the hydroxy groups of the diol with the reagent gives rise to some such formation as that depicted in *equ. 1*. The ring-closure itself occurs by a concerted mechanism, with intramolecular attack of the other hydroxy group of the diol, and with intramolecular S_N2 substitution. The process for an alkoxysulfonium salt is shown in *equ. 2*, on the example of 1,4-butanediol.



(2)

The above conclusions are supported by the following findings: *a)* The experimental facts observed during the reactions of the monohydroxy compounds (the dependence of the ether formation on the reactivity of the alcohol); *b)* The observations by *Mihailović* [8] [15] relating to the ring-closures of (±)- and *meso*-2,5-hexanediol in the presence of a large excess of DMSO: the transformation occurs with inversion of one of the chiral C-atoms; *c)* The non-occurrence of olefin formation in the case of diols containing only primary and secondary hydroxy groups; this indicates that a carbenium cation is not formed in the ring-closure; *d)* The appearance of dienes among the transformation products of ditertiary diols. In these compounds a role may be played in the transformation by the stable tertiary carbenium ion, which may be stabilized by proton release and thus by C,C-double-bond formation. Other causes, already discussed above, are also involved in diene formation. Literature data too [9] [10] point to the presence of the carbenium cation: the ring-closures of the more highly reactive (−)-4-methyl-1,4-hexanediol and (±)- and *meso*-1,4-diphenyl-1,4-butanediol in a large excess of DMSO are accompanied by racemization; *e)* The selectivity of formation of hexamethylene oxide in the case of 1,6-hexanediol. It is known from literature data that, in the transformations of 1,6-hexanediol [16] [17] and higher diol homologues under acidic conditions, *i.e.* when a protonated hydroxy group is produced, 5- and 6-membered cyclic ethers are formed as a consequence of the striving towards the development of a more stable carbenium ion; *f)* The reactivities of 1,2- and 1,3-diols and the observed reactions are similarly in accordance with the above conclusions. The low probability of formation of the 3- and 4-membered strained rings does not provide a possibility for cyclodehydration. With the disecondary compounds, therefore, there is merely a possibility for 1,2-elimination; this proceeds *via* the secondary carbenium ion, which is formed with low probability, it involves the cleavage of a strong C,H-bond, it is accordingly slow, and it thus results in a low conversion. On the other hand, the ditertiary compounds may be rapidly transformed to the corresponding products (unsaturated alcohols, dienes and oxo compounds) by 1,2-elimination and rearrangement *via* the stable tertiary carbenium cation.

2.4.2. *Role of acids in dehydration.* Our experimental results reveal that the above mechanism is not the only possibility for cyclodehydration. Literature data [18-21] indicate that the thermal decomposition of DMSO involving partial autoxidation leads to the formation of strong acids (methanesulfonic acid, sulfuric acid). As a consequence of the presence of these acids, all three of the above-

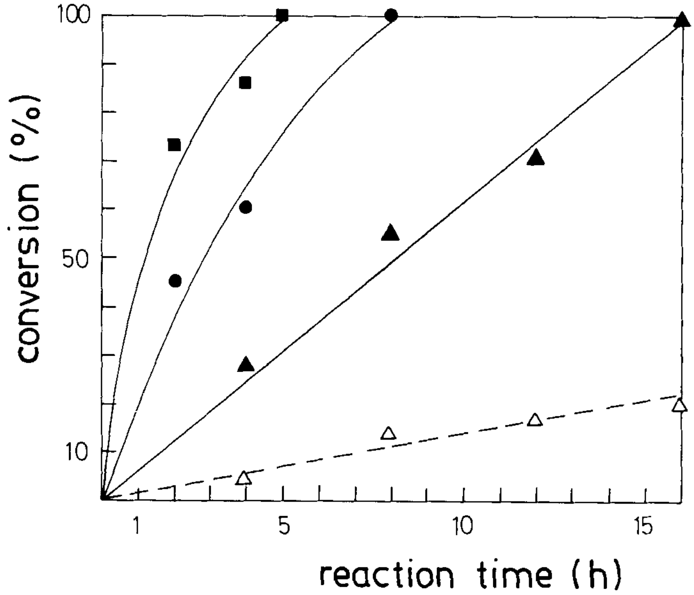


Fig. 1. *Transformation of 2,5-hexanediol at different reaction conditions* (method A, 195°); ■ in the presence of H_2O_2 (diol:DMSO:H_2O_2 mol ratio 16:1:1), in air; ● in the presence of H_2O (diol:DMSO:H_2O mol ratio 16:1:2), in air; ▲ without additive, in air; △ without additive, in nitrogen.

mentioned dehydration processes can also take place by a simple acid-catalyzed mechanism. Certain experimental facts confirm such acid-catalyzed transformations: *a)* In the overhelming majority of cases the aqueous phase of the reaction mixture is strongly acidic (pH = 1.0-3.0, determined by *'Multiphan'* narrow range indicator paper); *b)* If the dehydration is carried out in a nitrogen atmosphere, but under otherwise identical reaction conditions, in a given reaction time a much lower conversion is attained than in the presence of air *(Fig. 1)*. Similarly, if the reaction is carried out in parallel *via* methods A and C, under otherwise identical

Table 5. *Transformations of alcohols and diols in presence of DMSO and various additives*

Alcohol/diol	Reaction conditions[a]		Conversion [%]	Product distribution [mol %]	
	Additive, mol ratio	Time [h]			
1-Butanol	H_2O, 2	24	9	1-Butene	10
				Di-*n*-butyl ether	90
	H_2O_2, 1	16	42	1-Butene	5
				Di-*n*-butyl ether	90
				Unidentified	5
2-Butanol	H_2O, 2	24	0	-	
	H_2O_2, 1	12	100	Butenes	100
2,5-Hexanediol	Et_2NH, 1	16	0[b]	-	

[a] Alcohol/diol:DMSO mol ratio 16:1; temperature 195°; method A.
[b] At the end of reaction no DMSO could be detected.

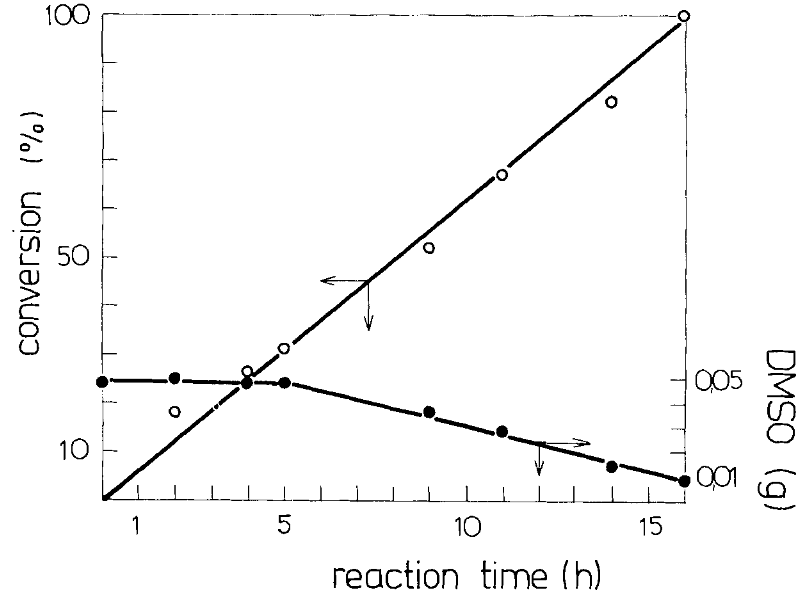


Fig. 2. *Variations in time of the diol conversion and the amount of DMSO in the transformation of 2,5-hexanediol* (diol: DMSO mol ratio 16:1, method A, 195°).

reaction conditions, in the latter case (*i.e.* when atmospheric oxygen is present in unrestricted amount as a possible oxidizing agent) a shorter reaction time is always sufficient for complete conversion to be attained (see *Table 1*, transformations of cyclohexanol and benzyl alcohol); *c)* The presence of an oxidizing agent (H_2O_2), which promotes acid formation by decomposition of the reagent, accelerates cyclodehydration *(Fig. 1)*, and the cases of 1- and 2-butanol permit the occurrence of a reaction which can not be observed at all in the absence of the additive *(Table 5)*; *d)* In the case of 2,5-hexanediol we studied the variations in time of the conversion and the amount of reagent. It may be seen from *Figure 2*, that the amount of reagent remains unchanged until about halfway through the reaction; it subsequently decreases, but it can still be detected even at the end of the reaction. It follows from this that initially the DMSO exerts its effects directly, in accordance with *equ. 1*; later, however, as the extent of the decomposition becomes over greater, the acids formed also play a role in the transformation. This is the first experimental evidence that two mechanisms may occur simultaneously during dehydration in DMSO.

3. Other comments. - The ring-closure does not occur in the presence of a base (diethylamine). This is due in part to the neutralization of the acids formed, and in part to the direct reaction of the base with the DMSO *(Table 5)*.

The acid formation is a complex process, dependent on many factors. It is influenced by the amount of oxygen in the vapour space, and probably also by certain of the products (*e.g.* water) formed in the reaction. The fact that, even after a long reaction time and with a relatively large amount of reagent, 1- and 2-butanol do not show any signs of transformation permits the conclusion that the acid concentration is very low in a pure reaction mixture containing only alcohol (diol) and DMSO, even in spite of prolonged heating. It is possible that at times no acid is formed at all, the dehydration then proceeding simply *via* one mechanism. This is suggested by the fact that in some exceptional cases the reaction mixture remained neutral (in such cases a longer reaction time was always required for 100% conversion). However, this phenomenon was observed only in an apparently random manner, and could not be brought into correlation with either the structures of the diols or the reaction conditions.

The reaction may also be accelerated by addition of water *(Fig. 1, Table 5)*. In all probability, water speeds up the reaction by promoting acid formation, but its role is not clear in every respect. For example, in the transformations of 1- and 2-butanol in the presence of water *(Table 5)*, acid could not be detected by our method.

These facts shed light on the cause of the apparent contradiction between the non-occurrence of intramolecular ether formation from primary and secondary alcohols and the occurrence of ether formation (ring-closure) in the case of diols containing primary and secondary hydroxy groups. In the case of alcohols, for steric reasons it is not favoured for the transition state formed between the reactant and the DMSO to undergo further transformation by nucleophilic substitution of another alcohol molecule. At the same time, with the diols, as a consequence of the favourable steric arrangement, there is a possibility for substitution by means of intramolecular attack of the other hydroxy group.

Experimental Part

The DMSO was dried with NaOH for 24 h, distilled in vacuum, and stored on 4A molecular sieve: b.p. 97–98°/25 Torr; $n_D^{20} = 1.4790$ (Lit. [22]: b.p. 83°/17 Torr; $n_D^{20} = 1.4795$).

1-Butanol, 2-butanol, *t*-butyl alcohol, cyclohexanol, benzyl alcohol and allyl alcohol were products of *Reanal*, and 2,3-butanediol, pinacol, 2,4-pentanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,5-hexanediol and 2,5-dimethyl-2,5-hexanediol were products of *Fluka*. The other compounds were synthesized by literature methods.

The conversion and the product composition were determined with a GC. method (*Carlo Erba* Mod. GV instrument, 1.2 m long *Carbowax* 20 M or *Reoplex* 400 column, 70–200°). Products were identified with the use of authentic comparative substances, and *via* IR. and NMR. spectra.

Dehydration methods employed:

Method A (for GC. examinations): 0.01 mol diol and the appropriate amount of DMSO (0.049 g, 0.000625 mol, for a diol:DMSO ratio of 16:1) are sealed in a 5 ml ampoule and heated at the desired temperature. After a suitable time, the reaction mixture is cooled, dried and chromatographed.

Method B (preparative-scale reaction): a mixture of 0.1 mol diol and 0.49 g (0.00625 mol) DMSO is kept at 180–200°. The products are distilled from the mixture either directly or after reflux during 10 h. The product in the cooled receiving vessel is separated from water, neutralized with K_2CO_3, washed 3 times with the same volume of ice/water, dried, distilled and chromatographed.

Method C (for transformations of alcohols): the appropriate mixture of alcohol and DMSO is refluxed. The conversion and product composition are determined by GC.

Each compound was run at least twice. The tables show the averages of the runs. The variation in the product ratios was less than 5%. All runs were made in air, except those the results of which are presented in *Figure 1*.

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