9. Lemal, D. M. and Fry, A. J. *Tetrahedron Letters* **1961** 775.
10. Simonsen, J. and Barton, D. H. R. *The Terpenes* (2nd Ed.) Vol. III. Cambridge 1951, p. 413.
11. Schuller, W. H. and Lawrence, R. V. *Chem. & Ind. London* **1961** 105.
12. Ref.[10], p. 374.
13. Ref.[10], p. 445.
14. Schuller, W. H., Moore, R. N. and Lawrence, R. V. *J. Am. Chem. Soc.* **82** (1960) 1734.
15. Ref.[10], p. 428.
16. Milne, G. W. A. and Smith, H. *Chem. & Ind. London* **1961** 1307.
17. Ireland, R. E. and Schiess, P. W. *Tetrahedron Letters* **1960** No. 25, 37.
18. Antkowiak, W., ApSimon, J. W. and Edwards, O. E. *J. Org. Chem.* **27** (1962) 1930.
19. Ireland, R. E. and Newbould, J. *J. Org. Chem.* **27** (1962) 1931.
20. Hammarberg, G. and Wickberg, B. *Acta Chem. Scand.* **14** (1960) 882.

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The Hydrolysis of 1,3-Dioxolan and Its Alkyl Derivatives. Part II. The Three Geometric Isomers of 2,4,5-Trimethyl-1,3-dioxolan

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In continuation of the previous study of the influence of structure on the kinetics of hydrolysis of derivatives of 1,3-dioxolan [1], the present paper describes the synthesis of, and kinetic data for the three geometric isomers of 2,4,5-trimethyl-1,3-dioxolan.

Experimental. The 2,3-butanediol employed in the synthesis of the examined dioxolans was a technical product (L. Light & Co., Ltd.) consisting mainly of the *meso* form. The *dl*-form present as an impurity was removed by careful distillation in a Todd precision fractionation assembly. Only the middle distillate, which crystallized in the receiver (b.p. 82—84°C/8 mm Hg; $n_D^{25} = 1.4370$), was employed in the subsequent syntheses. The pure *meso*-2,3-butanediol could be employed directly for the preparation of two geometric isomers of 2,4,5-trimethyl-1,3-dioxolan, but the *dl*-2,3-butanediol required in the synthesis of the third isomer was obtained from the *meso* form by the following reaction sequence:

$$\textit{meso}\text{-2,3-butanediol} \xrightarrow{Ac_2O} \textit{meso}\text{-2,3-butanediol diacetate} \xrightarrow{HBr} \textit{dl}\text{-2,3-dibromobutane} \xrightarrow{\text{Ag acetate}} \xrightarrow{\text{alkaline hydrolysis}} \textit{dl}\text{-2,3-butanediol}$$

The diacetate of *meso*-2,3-butanediol and *dl*-2,3-dibromobutane were prepared as described by Wilson and Lucas [2], whereas the preparation of *dl*-2,3-butanediol diacetate and *dl*-2,3-butanediol took place in principle by the method described by Winstein and Buckles [3]. All the intermediates and the final product *dl*-2,3-butanediol (b.p. 80°C/5 mm Hg) were carefully purified by fractional distillation.

The isomers of 2,4,5-trimethyl-1,3-dioxolan were prepared from acetaldehyde *n*-amyl acetal and the 2,3-butanediols by a procedure similar to that used to prepare 2,4-dimethyl-1,3-dioxolans [1]. The 2,*cis*-4,*trans*-5-trimethyl-1,3-dioxolan obtained from *dl*-2,3-butanediol had the following physical constants: b.p. 103.2°C/749.9 mm Hg, $n_D^{25} = 1.3922$, $d_4^{25} = 0.8894$, $[R]_{obs.} = 31.11$ ($[R]_{calc.} = 30.84$).

When *meso*-2,3-butanediol was the starting material, a mixture of 2,*cis*-4,*cis*-5-trimethyl-1,3-dioxolan and 2,*trans*-4,*trans*-5- trimethyl-1,3-dioxolan resulted. The components of the mixture were separated by careful fractional distillation. The physical properties of the lower-boiling component, which was the 2,*cis*-4,*cis*-5-form on the basis of kinetic and other data, were b.p. 109.5°C/751.0 mm Hg, $n_D^{20} = 1.4007$, $d_4^{20} = 0.9123$, $[R]_{obs.} = 30.91$ ($[R]_{calc.} = 30.84$) and those of the higher-boiling component, 2,*trans*-4,*trans*-5-trimethyl-1,3-dioxolan, b.p. 112.4°C/753.4 mm Hg, $n_D^{20} = 1.4038$, $d_4^{20} = 0.9201$, $[R]_{obs.} = 30.87$ ($[R]_{calc.} = 30.84$). The purities of the synthesized 2,4,5-trimethyl-1,3-dioxolans were checked by gas-chromatographic analysis.

The kinetic measurements were carried out as described previously [1].

The rate coefficients of the acid-catalyzed hydrolysis of the three isomers and kinetic quantities calculated from them are shown in Table 1. The assignations of the structures of the isomers were made on the

Table 1. Values of the rate coefficients k (l mole^{-1}s^{-1}), activation energy E (kcal/mole), logarithm of the frequency factor (log A) and activation entropy $\Delta S^{\ddagger}$ (E.U.) for the acid-catalyzed hydrolysis of the geometric isomers of 2,4,5-trimethyl-1,3-dioxolan.

Parent glycol	Dioxolan	°C	$10^4 \cdot k$	E	log A	$\Delta S^{\ddagger}$
dl-2,3-Butanediol	2,*cis*-4,*trans*-5-Trimethyl-1,3-dioxolan	25	67.8 ± 0.5			
—»—	—»—	35	225 ± 2	21.40	13.52	+ 1.37
—»—	—»—	45	656 ± 7			
meso-2,3-Butanediol	2,*cis*-4,*cis*-5-Trimethyl-1,3-dioxolan [a]	15	30.1 ± 0.2			
—»—	—»—	25	108 ± 1	22.49	14.52	+ 5.93
—»—	—»—	35	363 ± 3			
—»—	2,*trans*-4,*trans*-5-Trimethyl-1,3-dioxolan [b]	15	7.50 ± 0.04			
—»—	—»—	25	24.6 ± 0.2	22.77	14.11	+ 4.05
—»—	—»—	35	93.3 ± 1.1			

[a] the lower-boiling isomer. [b] the higher-boiling isomer.

basis of the following independent information.

The effect of polarity on the rate of hydrolysis is naturally the same for all three isomers and therefore the differences in their rates of hydrolysis must be mainly due to steric factors associated with the opening of the dioxolan ring by the *A 1* mechanism of acetal hydrolysis. In accordance with the explanation of the steric effects suggested previously [1], it may be assumed that the rates of hydrolysis of the three isomers increase in the sequence: 2,*trans*-4,*trans*-5-trimethyl-1,3-dioxolan < 2, *cis*-4,*trans*-5-trimethyl-1,3-dioxolan < 2, *cis*-4,*cis*-5-trimethyl-1,3-dioxolan. This sequence is valid at least as far as the second isomer is concerned because its structure follows from its synthesis from *dl*-2,3-butanediol (Table 1). The structures of the other two isomers derived from *meso*-2,3-butanediol are confirmed, apart from the kinetic data, by their physical constants as compared with those of the isomers of 2,4-dimethyl-1,3-dioxolan [1]. Of the latter isomers, the lower-boiling isomer (the *cis* form) hydrolyzed more rapidly and had a lower density and lower refractive index than the higher-boiling isomer and the same applies to the dioxolans derived from *meso*-2,3-butanediol. In addition, one must expect on the basis of the steric effects discussed earlier [1] that the 2,*trans*-4,*trans*-5-trimethyl-isomer is less likely to hydrolyze more rapidly than the *trans* isomer of 2,4-dimethyl-1,3-dioxolan. This is borne out by the rate coefficients at 25°C, which are 5.07×10^{-3} l mole^{-1}s^{-1} for the latter and 2.46×10^{-3} l mole^{-1}s^{-1} for the former compound.

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1. Salomaa, P. and Kankaanperä, A. *Acta Chem. Scand.* **15** (1961) 871.
2. Wilson, C. E. and Lucas, H. J. *J. Am. Chem. Soc.* **58** (1936) 2396.
3. Winstein, S. and Buckles, R. E. *J. Am. Chem. Soc.* **64** (1942) 2780, 2787.

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