residue was diluted with 60 ml. of pentane and washed several times with water to remove residual pyridine, then again dried over magnesium sulfate and evaporated under vacuum. The liquid residue, free of pyridine odor, was dissolved in 10 ml. of pentane and cooled with a mixture of Dry Ice and methylene chloride. After about 2 hr., colorless crystals separated which were collected by filtration, m.p. 55–57°. Further recrystallizations from pentane raised the melting point to 67.5–68.5°. The total weight of solid isolated was 1.23 g. (60%).

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.60; H, 7.67.

An infrared spectrum of this solid showed no hydroxyl or carbonyl absorptions. An n.m.r. spectrum showed the characteristic phenyl absorption at 2.5–2.9 (area, 5.0), a singlet at 6.70 (area, 3.0), and two sharp singlets at 8.70 (area, 6.2) and 8.80 τ (area, 5.9).

A chloroform solution of 0.52 g. of the ortho ester was shaken for a few minutes with 3 *N* hydrochloric acid and then washed with 5% aqueous sodium hydroxide solution. The organic phase was dried over magnesium sulfate and evaporated to give 0.41 g. of solid, m.p. 90–92°, after recrystallization from pentane. This solid was identified as *cis*-hydroxybenzoate (**2b**) by its infrared spectrum and lack of melting point depression when mixed with an authentic sample.

Solvolytic Studies of *cis*- and *trans*-2,2,4,4-Tetramethylcyclobutane Derivatives[1]

CHARLES F. WILCOX, JR., AND DAVID L. NEALY[2]

Department of Chemistry, Cornell University, Ithaca, New York

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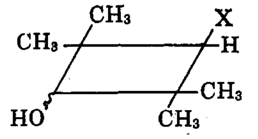
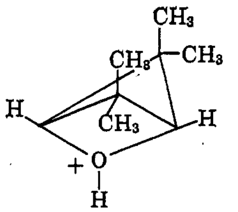
Several 2,2,4,4-tetramethylcyclobutane esters have been solvolyzed and the rates and products determined. No evidence is found for participation of a 3-OH group but the results are consistent with a cyclopropylcarbinyl intermediate. The mechanisms of the solvolyses are discussed and related to the previous work on the dehydration of the 2,2,4,4-tetramethylcyclobutane-1,3-diols.

Recently Hasek, Clark, and Chaudet reported that cleavage of *cis*- and *trans*-2,2,4,4-tetramethylcylobutane-1,3-diols (**1a**) by aqueous acid proceeded at markedly different rates.[3] They proposed that the *trans*-diol reacted with neighboring hydroxyl participation by way of the bicyclic oxonium salt **2** which they felt possessed sufficient stability to account for the higher reactivity of the *trans*-diol.



1a, X = OH
1b, X = *p*-toluenesulfonate



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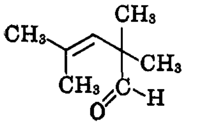
We were interested in examining this system in part because of our general interest in bicyclic systems and in part because of our thwarted attempts to carry out related cyclizations on less strained systems.[4] A quantitative estimate of the relative reactivities of the *cis*- and *trans*-diols seemed difficult to obtain from the dehydration reaction.[5] On the plausible assumption that the *cis*- and *trans*-hydroxy tosylates (**1b**) would possess a similar difference in reactivity these esters were prepared and studied. From the kinetic and product data obtained with these esters combined with similar data for model systems and other derivatives of **1a**, it could be shown that the intermediacy of bicyclic ion **2** is improbable. An alternative mechanism consistent with all data now available will be presented.

Dehydration of the Diols.—The dehydration of *cis*- and *trans*-2,2,4,4-tetramethylcyclobutane-1,3-diol in 4% aqueous sulfuric acid was repeated. In addition to 2,2,4-trimethyl-3-pentenal (**3**), reported to be the major product by previous workers, two other higher boiling materials were isolated. These proved to be the cyclic hemiacetal **4** and the bisacetal **5**.[6] Since these products appear to be formed from **3** rather than **1a** and since their identification involves considerable chemistry not pertinent to the present cyclobutanediol problem, they will be discussed elsewhere.[7] As reported by Hasek, *et al.*,[3] the organic material precipitating from the acid solution was found to be almost pure *cis*-2,2,4,4-tetramethylcyclobutane-1,3-diol. No evidence for other primary rearrangement products was found.



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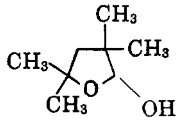

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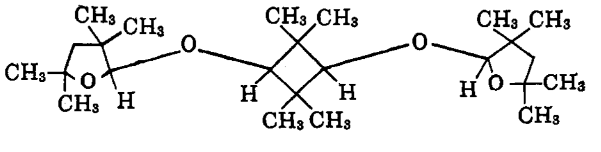

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Synthesis of Esters for Solvolytic Studies.—Treatment of pure *cis*-2,2,4,4-tetramethylcyclobutane-1,3-diol with one equivalent of *p*-toluenesulfonylchloride in pyridine gave a 58% yield of the *cis*-hydroxytosylate and a 10% yield of the *cis*-ditosylate. Pure *trans*-diol when treated in the same manner gave a 35% yield of the *trans*-hydroxytosylate and an 8% yield of *trans*-ditosylate. Because the diesters proved to have such

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(1) Taken from the dissertation submitted by D. L. N. in partial fulfillment of the requirements for the Ph.D. degree, Cornell University, June, 1963.

(2) National Science Foundation Predoctoral Fellow, 1959–1963.

(3) R. H. Hasek, R. D. Clark, and J. H. Chaudet, *J. Org. Chem.*, **26**, 3130 (1961). The *cis*-diol was essentially unchanged by an acid treatment that completely cleaved the *trans*-diol.

(4) C. F. Wilcox, Jr., and S. S. Chibber, *ibid.*, **27**, 2332 (1962).

(5) With the high concentrations employed the dehydrations are heterogeneous. Under conditions where the *trans*-diol reacted completely, the *cis*-diol was recovered unchanged; however, under much more vigorous conditions, the *cis*-diol reacted to give intractable products.

(6) The stereochemistry of the bisacetal **5** is uncertain.

(7) C. F. Wilcox, Jr., and D. L. Nealy, *J. Org. Chem.*, **28**, 3454 (1963).

TABLE I

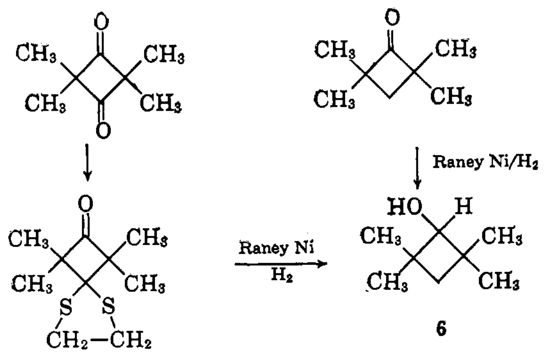
SOLVOLYSIS RATE CONSTANTS

Compound	Temp., °C.	Solvent	k_1, sec.$^{-1}$	ΔH^*, kcal.	ΔS^*, e.u.
trans-2,2,4,4-Tetramethylcyclobutane-1,3-diol monotosylate	85.0	90% acetone–water	1.10×10^{-3}		
	75.0	90% acetone–water	4.10×10^{-4}	+24.5	−4.1
	50.2	90% acetone–water	2.48×10^{-5}		
cis-2,2,4,4-Tetramethylcyclobutane-1,3-diol monotosylate	115.0	90% acetone–water	3.14×10^{-5}		
	100.0	90% acetone–water	6.98×10^{-6}	27.7	−8.5
	85.0	90% acetone–water	1.41×10^{-6}		
	75.0	90% acetone–water	5.12×10^{-7}		
2,2,4,4-Tetramethylcyclobutyl tosylate	75.0	90% acetone–water	6.31×10^{-4}		
	50.1	90% acetone–water	4.61×10^{-5}	23.7	−5.2
	25.0	90% acetone–water	1.86×10^{-6}		
trans-2,2,4,4-Tetramethylcyclobutane-1,3-diol ditosylate	115.0	71.4% acetone–water	4.9×10^{-6}		
cis-2,2,4,4-Tetramethylcyclobutane-1,3-diol ditosylate	115.0	71.4% acetone–water	$<10^{-8}$		
trans-3-Tosyloxy-2,2,4,4-tetramethylcyclobutyl *p*-nitrobenzenesulfonate	121.8	55.5% acetone–water	2.86×10^{-4}		
cis-3-Tosyloxy-2,2,4,4-tetramethylcyclobutyl *p*-nitrobenzenesulfonate	121.8	55.5% acetone–water	2.2×10^{-7}		

a low solvolytic reactivity, more reactive mixed esters were prepared by treating the pure *cis*- and *trans*-hydroxytosylates with *p*-nitrobenzenesulfonyl chloride in pyridine. All of these arylsulfonate esters had the expected elemental compositions and their infrared spectra were consistent with the assigned structures.

The desirable reference alcohol, 2,2,4,4-tetramethylcyclobutanol (6), had not been described previously. It was prepared by two routes, which are outlined in Chart I. The monoketone was a known compound.[8] Confirmation of the structure of alcohol 6 was obtained from its infrared and n.m.r. spectra. It was converted smoothly with *p*-toluenesulfonyl chloride in pyridine into a solid tosylate.

CHART I



Solvolyses.—The kinetics of solvolysis of the various arylsulfonate esters in aqueous solvents were determined by the sealed ampoule technique. Good first-order kinetic behavior was observed in all runs. The rate data are summarized in Table I.

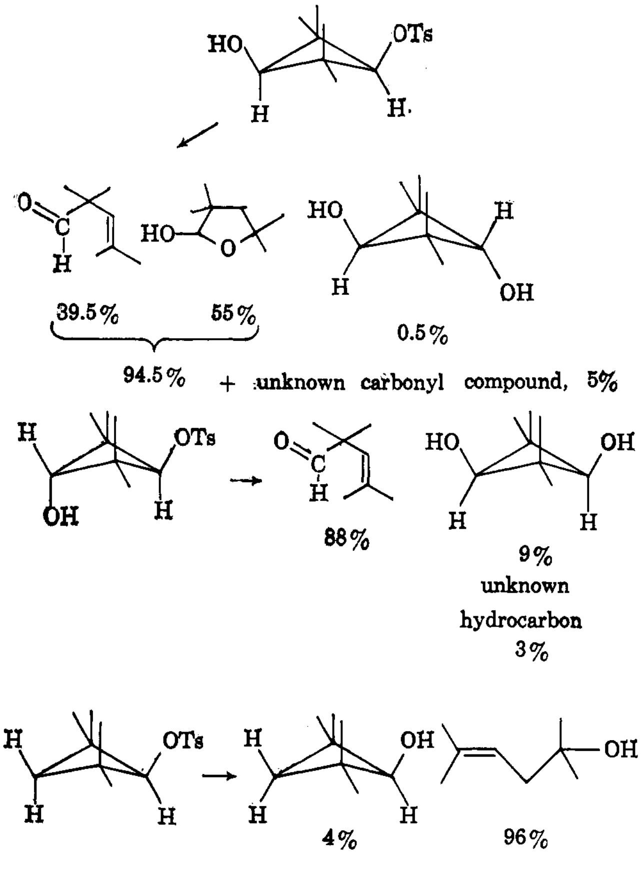
The solvolysis products from the first three *p*-toluenesulfonates were analyzed by gas–liquid chromatography. Each component was collected separately and identified. The results are summarized in Chart II.

Discussion

The monotosylates show a *trans*/*cis* rate ratio at 75° of *ca.* 800 which is a quantitative measure of the *trans*-hydroxyl effect noted by Hasek, *et al.* This could be taken as support for the participation of a neighboring *trans*-hydroxyl group, but several pieces of the new evidence suggest that this interpretation may be inadequate. First, it is striking that the *trans*- and *cis*-diesters show an equally large rate ratio. It is highly improbable that a neighboring tosyloxy group, if it participated at all, would give the same large effect. A further difficulty is the formation in 9% yield of *cis*-1,3-dihydroxy-2,2,4,4-tetramethylcyclobutane from the *trans*-hydroxy ester. It would be expected in analogy to other examples of participation that a

CHART II

PRODUCT ANALYSES



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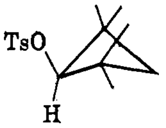
[8] H. L. Herzog and E. R. Buchman, *J. Org. Chem.*, **16**, 99 (1951).

bridged intermediate such as **2** would give retention of configuration.

Stronger evidence against **2** comes from the product and rate data for the unsubstituted mono tosylate of alcohol **6**. The major product (96% of isolated material) is the rearranged alcohol 2,5-dimethyl-3-hexen-2-ol. Formation of rearranged alcohol is readily understood in terms of the set of ions associated with a nonclassical cyclopropylcarbinyl intermediate.[9] Support for such an intermediate is provided by comparing the solvolytic rate of the unsubstituted monoester **7** with that of 7-norbornyl *p*-toluenesulfonate (**8**). Bicyclic ester **8** has a similar pattern of substitution adjacent to the reaction site as well as a similar ground state bond angle (*ca.* 90°) at this point.[10] The large rate ratio of $3 \times 10^9{:}1$ (**7**/**8**, probably a minimum figure because of the slightly larger angle in **8**) is an indication of the importance neighboring group participation plays in accelerating this cyclobutyl tosylate.[11,12]



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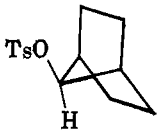

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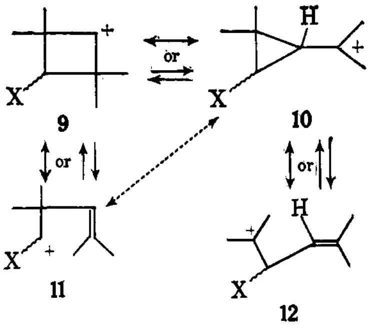
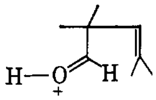
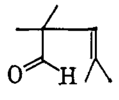
Since the rate of **7** is so similar to the rate of *trans* **1b** it seems probable that both proceed by related mechanisms. In fact, since all of the esters in Table I show markedly enhanced rates compared to the bicyclic model, it can be inferred that all involve something special.[13] A rate enhancement of 10^9 is without precedent for neighboring hydroxyl participation.

Invoking a cyclopropylcarbinyl intermediate for all of the esters has its complications, but a rational picture can be sketched. It is plausible that substitution of a tosyloxy group for hydrogen (X = OTs) could cause the observed large retardation in rate because of its unfavorable inductive effect. This would be particularly true if structure **11** were important in the transition state. Substitution of a hydroxy group for hydrogen (X = OH) should have an analogous, though smaller, unfavorable inductive effect, but this could easily be compensated for by increased importance of **11** and **11a**. Intermediacy of **11a** would account for the production of **3** (and products derived from it) in major amounts. The same set of intermediates could account for the formation of *trans*-diol from *cis*-monotosylate and *cis*-diol from *trans*-monotosylate.





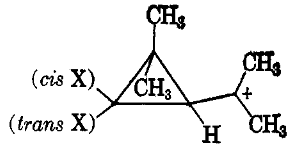
11a



3

The working hypothesis of cyclopropylcarbinyl intermediates can be extended to account for the large and similar *trans*/*cis* rate ratios of the mono- and diesters. The nearly identical ratios suggest a steric origin.[14] It is accepted that cyclobutanes are puckered[15] so that the *trans*-esters containing one pseudoaxial X group should be significantly less stable than the *cis*-esters. It has been determined that *cis*-methyl-3-methylcyclobutanecarboxylate is slightly more stable than the *trans* isomer (K_{eq} = 1.6).[16] The difference might be magnified in **1** by the four flanking methyl groups.

In addition to this ground state contribution to a *trans*/*cis* rate effect, models suggest that in a cyclopropylcarbinyl transition state the relative stabilities of the *cis* and *trans* species are inverted. This can be seen most clearly by examining the interactions of the substituents in a fully formed cyclopropylcarbinyl intermediate. The *cis* isomer would produce an ion with the hydroxyl or tosyloxy group on the same side of the cyclopropane ring as the large dimethylcarbinyl cation whereas the *trans* isomer places the X group on the less hindered side. The combined ground state and transition state effects work in the direction of the observed *trans*/*cis* ratio but whether they are quantitatively sufficient will have to remain in doubt until appropriate model compounds have been equilibrated.[17]



We have not rigorously proved the involvement of a cyclopropyl carbinyl intermediate in the solvolysis of the diesters and the hydroxy esters; however, such an intermediate can account reasonably well for the rates

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[9] No attempt will be made in this paper either to distinguish between resonance and equilibrium in a cyclopropylcarbinyl intermediate or to distinguish between an intermediate and transition state. Although the same name "cyclopropylcarbinyl intermediate" will be employed in the later discussion of the solvolysis of substituted cyclobutyl derivatives it should be understood that the detailed geometry and balance between the various forms of the ion undoubtedly differ for each case.

[10] C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960); P. von R. Schleyer and R. D. Nicholas, *ibid.*, **83**, 183 (1961).

[11] This ratio was derived by first correcting the rate of **7** given in Table I for the change in solvolytic conditions of acetone–water at 50° to acetic acid at 25°. The correction factor of 0.37 was obtained from the solvolysis of 2,2,4-trimethyl-3-penten-1-ol *p*-toluenesulfonate under both conditions. The latter tosylate has been shown to proceed through a similar cyclopropylcarbinyl intermediate.[7]

[12] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).

[13] Even the slowest ester, the *cis*-ditosylate, would appear to be faster than the model bicyclic ester by a factor of 30. This is likely to be a minimum factor since it does not include the effect of a somewhat larger angle in **8**[11] or the absence of an unfavorable inductive effect.

[14] For [2.2.1]bicyclic systems it has been suggested that steric effects are largely determined by the atom directly attached to the ring; C. F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

[15] In the closely related *cis*- and *trans*-1,3-dicyano-2,2,4,4-tetramethylcyclobutanes it has been estimated from dipole moment measurements that the *cis* isomer deviates from coplanarity by 30–40° and the *trans* isomer by at least 18°; F. Lautenschlaeger and G. F. Wright, *Can. J. Chem.*, **41**, 863 (1963).

[16] J. M. Conia, N. L. Allinger, J. Ripoll, L. A. Tushaus, and C. L. Neumann, *J. Am. Chem. Soc.*, **84**, 4983 (1962).

[17] Another potential explanation for the *trans*/*cis* ratio is in terms of electrostatic interaction of the X substituent with the developing charge (field effect). Models suggest that with a puckered cyclobutane this effect is nearly the same for both isomers.

and products. The new evidence offered here would be difficult to explain in terms of the previously proposed bicyclic intermediate.

Experimental[18]

Dehydration of 2,2,4,4-Tetramethylcyclobutane-1,3-diol (1a).—Dehydration of commercial diol 1a (Eastman) was effected according to the procedure of Hasek, *et al.*[3] In addition to the reported[3] major product, 2,2,4-trimethyl-3-pentenal, two minor products were isolated by distillation and chromatography on alumina of the higher boiling fractions. The first, a solid, b.p. 110–111° (76 mm.), m.p. 53.2–54.0°, has been identified as 3,3,5,5-tetramethyltetrahydro-2-furanol.[7] The second, m.p. 59–60°, was a very high boiling compound tentatively identified as *O,O'*-bis(3,3,5,5-tetramethyltetrahydro-2-furyl)-2,2,4,4-tetramethylcyclobutane-1,3-diol on the basis of its elemental analysis and n.m.r. spectrum.

Anal. Calcd. for $C_{24}H_{44}O_4$: C, 72.67; H, 11.18. Found: C, 72.76; H, 11.14.

The n.m.r. spectrum of this compound consisted of sharp peaks at 5.70 and 6.56, a quartet (J = 13 c.p.s.) centered at 8.33, and a series of several peaks of unequal intensities at 8.74–9.02 τ with relative areas of 2.0:2.0:4.0:36.6.

***cis*-2,2,4,4-Tetramethylcyclobutane-1,3-diol Mono- and Di-*p*-toluenesulfonates.**—Eastman 2,2,4,4-tetramethylcyclobutane-1,3-diol was separated by the method of Hasek, *et al.*,[19] into pure *cis*-diol, m.p. 161–162°, and *trans*-diol, m.p. 147–148°. To a solution of 40 g. of pure *cis*-diol 1a in 400 ml. of dry pyridine at 0° was added 53 g. of recrystallized *p*-toluenesulfonyl chloride. The solution was left at room temperature for 25 hr., then cooled to 0°, poured into 1.5 l. of ice–water, stirred well, and filtered. The solid was washed once with cold, dilute hydrochloric acid, dried in air, and extracted with ether. The ether extract was evaporated, and the residue recrystallized from ether–hexane to give 48 g. (58%) of *cis*-monoester 1b, m.p. 111.0°–112.0°.

Anal. Calcd. for $C_{15}H_{22}O_4S$: C, 60.32; H, 7.43, S, 10.73. Found: C, 60.92; H, 7.64; S, 10.53.

The solid residue from the ether extraction was recrystallized from carbon tetrachloride to give 12.0 g. (10%) of diester, m.p. 171.5–172.5°.

Anal. Calcd. for $C_{22}H_{28}O_6S_2$: C, 58.40; H, 6.23; S, 14.17. Found: C, 58.08; H, 6.21; S, 14.40.

This diester showed strong infrared absorption at 1600 but no hydroxyl absorption in the 3000–3800-cm.$^{-1}$ region.

***trans*-2,2,4,4-Tetramethylcyclobutane-1,3-diol Mono- and Di-*p*-toluenesulfonates.**—The pure *trans*-diol 1a was treated with *p*-toluenesulfonyl chloride in pyridine exactly as in the preceding preparation of the *cis*-esters. From 20 g. of diol was obtained 14.4 g. (35%) of a crystalline monoester, m.p. 96.0–96.8°.

Anal. Calcd. for $C_{15}H_{22}O_4S$: C, 60.32; H, 7.43; S, 10.73. Found: C, 60.34; H, 7.44; S, 10.71.

The monoester showed strong infrared absorption at 3580 (hydroxyl) and at 1600 cm.$^{-1}$.

In addition, 5.3 g. (8.4%) of a less-soluble ester, m.p. 195.0–196.0°, was isolated. This diester showed no hydroxyl absorption in its infrared spectrum.

Anal. Calcd. for $C_{22}H_{28}O_6S_2$: C, 58.40; H, 6.23; S, 14.17. Found: C, 57.92; H, 6.23; S, 13.77.

***cis*-3-Tosyloxy-2,2,4,4-tetramethylcyclobutyl *p*-Nitrobenzenesulfonate.**—To a solution of 5.0 g. of *cis*-monotosylate 1b in 100 ml. of ice-cold pyridine was added 5.0 g. of *p*-nitrobenzenesulfonyl chloride, m.p. 75–77°. After 3 days at room temperature, the solution was poured into 500 ml. of cold water, stirred, and filtered. The solid was washed with cold, dilute hydrochloric acid and water. Extraction of the solid with hot carbon tetrachloride removed unchanged starting materials. The residue, on recrystallization from acetone–water, afforded 3.7 g. (46%) of mixed ester, m.p. 206–207°. Infrared absorption was noted at 1600 and 1540 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{25}NO_8S_2$: C, 52.15; H, 5.21; N, 2.90; S, 13.26. Found: C, 52.49; H, 5.38; N, 2.72; S, 13.66.

***trans*-3-Tosyloxy-2,2,4,4-tetramethylcyclobutyl *p*-Nitrobenzenesulfonate.**—This mixed ester was prepared from *trans* 1b by the previous procedure for the *cis* mixed ester, and was isolated in the same way in 22% yield, m.p. 164–165° dec. The infrared spectrum of this diester was distinct from that of its *cis* isomer, but showed the expected absorption at 1600 and 1540 cm.$^{-1}$.

2,2,4,4-Tetramethylcyclobutanone.—This ketone was obtained by the method of Herzog and Buchman,[8] b.p. 128–129° (748 mm.), $n^{25}\text{D}$ 1.4122, lit.[8] b.p. 129° (745 mm.). Strong infrared absorption was noted at 1780 cm.$^{-1}$. The n.m.r. spectrum of this ketone showed two sharp peaks at 8.26 and 8.87 τ with relative areas 2.0:11.9, respectively.

2,2,4,4-Tetramethylcyclobutanol (6). Method A.—A solution of 7.1 g. of 2,2,4,4-tetramethylcyclobutanone in 150 ml. of absolute methanol was hydrogenated over W-4 Raney nickel[20] at room temperature and 2–4 atm. for 36 hr. After filtration, the solvent was distilled carefully through a 30-cm. column packed with glass helices. The residue crystallized on cooling to give 6.2 g. (86%) of crude alcohol, m.p. 54–56°. Recrystallization from isopentane afforded 5.8 g. of solid, m.p. 56.5–57.5°. Its infrared spectrum showed strong absorption at 3330, but no absorption in 1500–2000-cm.$^{-1}$ region. Its n.m.r. spectrum consisted of singlets at 6.45 and 7.78 and partially resolved doublets at 8.56 and 8.89 τ with relative areas of 1:1:2:12, respectively. A 3,5-dinitrobenzoate ester was prepared and recrystallized from 95% ethanol, m.p. 133.8–134.6°.

Method B.—To a cold solution of 10.0 g. of 2,2,4,4-tetramethylcyclobutane-1,3-dione (Eastman) and 7.0 g. of ethanedithiol in 60 ml. of glacial acetic acid was added 8.0 ml. of boron trifluoride etherate.[21] After 24 hr. at room temperature, the solution was warmed at 40° for 1 hr., cooled, diluted with 200 ml. of ether, extracted with eight 100-ml. portions of 5% sodium hydroxide solution, then with water, and dried over magnesium sulfate. After removal of solvent, 10.3 g. of liquid residue was obtained. The residue was refluxed for 72 hr. with 100 g. of freshly prepared W-4 Raney nickel[20] in 400 ml. of absolute ethanol. Filtration and distillation afforded 2.2 g. of the solid alcohol, m.p. 55–56° (24% yield from the dione). This alcohol was shown to be identical with that from method A by comparison of infrared spectra and by determination of mixture melting point.

2,2,4,4-Tetramethylcyclobutyl *p*-Toluenesulfonate (7).—This ester was prepared by the procedure used for conversion of diols 1a into tosylates. The crude solid ester was recrystallized from hexane to give 4.2 g. (63%) of colorless needles, m.p. 76.2–76.8°.

Anal. Calcd. for $C_{15}H_{22}O_3S$: C, 63.79; H, 7.85; S, 11.35. Found: C, 63.87; H, 7.95; S, 11.39.

Solvolysis Rate Determinations.—Mallinckrodt A.R. acetone was refluxed for 8 hr. over potassium permanganate and Drierite, and distilled from fresh Drierite. Nine volumes of a center fraction were combined with one volume of distilled water at 25.0° to form 90% (v./v.) acetone–water. The kinetics of solvolysis of the arylsulfonate esters were determined by the sealed ampoule technique. In the case of the monoesters, 5.00-ml. aliquots of a solution of about 0.03 *M* ester in 90% acetone–water were sealed in ampoules, placed in a constant temperature bath, quenched at intervals by cooling in ice-water, and titrated against a standard solution of sodium methoxide in absolute methanol to a bromthymol blue end point. Experimental infinity values agreed with calculated values to within ±2%. Each reaction was followed to 80% completion for at least one temperature.

In the case of the less-soluble diesters, a 5.00-ml. aliquot of 0.02–0.03 *M* solution of the diester in acetone was added to the appropriate volume of distilled water in an ampoule, and the ampoule was sealed. The diesters precipitated from the mixed solvents, but at the temperatures used for the solvolyses they were found to redissolve completely (with intermittent shaking) within 1 min. after being placed in the bath. Due to the very slow solvolysis rates of the *cis*-diesters, calculated infinity titers were used for the kinetic plots in these cases, but all reactions were followed to at least 60% reaction except for that of the *cis*-ditosylate. For this diester under all conditions used, the very slow rate could not be distinguished from the development of acidity in ampoules containing only solvent. Therefore, only a maximum rate could be estimated in this case.

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[18] Melting points are corrected. Infrared spectra of solids were taken with potassium bromide pellets and those of liquids with the pure liquids unless otherwise noted. N.m.r. spectra were determined on a Varian A-60 analytical spectrometer using an HR60 magnet. N.m.r. spectra of solids were determined with carbon tetrachloride solutions, and those of liquids with pure liquid unless otherwise noted.

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Solvolysis Products from *cis*-Mono-*p*-toluenesulfonate 1b.—A solution of 6.0 g. of *cis*-monoester **1b** in 150 ml. of 75% acetone–water was heated at 100° for 30 hr. in the presence of powdered calcium carbonate. The cooled solution was diluted with ether, washed with saturated sodium chloride solution and with 5% sodium carbonate solution, dried, and concentrated to a volume of about 5 ml. The residue was separated by g.l.c. on a preparative 20% silicon oil column at 135° into solvents, mesityl oxide, and the following solvolysis products, given together with their retention times: 2,2,4-trimethyl-3-pentenal (39.5%), 3.9 min.; 3,3,5,5-tetramethyltetrahydro-2-furanol (55.0%), 6.45 min.; *trans*-2,2,4,4-tetramethylcyclobutane-1,3-diol (0.5%), 10.0 min.; and an unidentified carbonyl-containing compound (5.0%), 14.2 min. All the previously named products were identified by comparison of infrared spectra and retention times with those of authentic samples.

Solvolysis Products from *trans*-Mono-*p*-toluenesulfonate 1b.—A solution of 4.50 g. of *trans*-ester **1b** in 120 ml. of 90% acetone–water was heated at 75° for 6 hr. in the presence of powdered calcium carbonate. The solvolysis products were isolated exactly as in the case of *cis* **1b**. The amount and retention time of each product on the same column at 150° are an unidentified volatile compound (3%), 1.62 min.; 2,2,4-trimethyl-3-pentenal (88%), 2.56 min.; and *cis*-2,2,4,4-tetramethylcyclobutane-1,3-diol (9%), 6.5 min. The two latter products were identified by comparison of infrared spectra and retention times with those of authentic samples. The identity of the solid diol was further confirmed by determination of its mixture melting point with a known sample.

In a control experiment, a solution of 0.50 g. of *trans*-diol **1a** in 20 ml. of 90% acetone–water containing 1.2 g. of *p*-toluenesulfonic acid (0.31 N acid) was heated for 4 hr. at 100°. The solution was cooled, diluted with ether, neutralized, and dried with sodium hydroxide pellets, filtered, and evaporated. The solid residue was washed with 10 ml. of benzene and dried in air to give 0.45 g. of solid, m.p. 144.0–145.5°. The infrared spectrum of this solid was identical with that of the starting *trans*-diol **1a**. In another control experiment, it was shown that under the conditions of the g.l.c. separation of solvolysis products, *trans*-diol **1a** could be collected unchanged in 80% yield.

Solvolysis Products from 2,2,4,4-Tetramethylcyclobutyl *p*-Toluenesulfonate (7).—A solution of 0.516 g. of the ester **7** in 85% acetone–water was heated at 75° for 5 hr. The cooled solution was diluted with ether, extracted twice with 6 N sodium hydroxide solution, once with water, dried, and concentrated to a volume of about 5 ml. The residue was separated by g.l.c. on a preparative 20% silicon oil column at 110° into solvent and two products, which were 2,2,4,4-tetramethylcyclobutanol (4%), 4.5 min.; and a liquid alcohol (96%), 5.6 min. This liquid, n^{25}_{D} 1.4440, reacted with bromine in carbon tetrachloride and with aqueous permanganate. It was shown to be 2,5-dimethyl-4-hexen-2-ol by comparison of infrared and n.m.r. spectra, and g.l.c. retention time with those of an authentic sample, described subsequently.

2,5-Dimethyl-4-hexen-2-ol.—2,5-Dimethylhexane-2,5-diol was prepared from 2,5-hexanedione and methylmagnesium iodide in 50% yield, m.p. 87.5–88°, lit.[22] m.p. 87–88°. Partial dehydration of the diol was effected by the procedure of Favorskaya and Ryzhoba.[22] From distillation of a solution of 30 g. of diol in 400 ml. of 0.03 N sulfuric acid was obtained 25 g. of organic distillate, which was separated by fractional distillation into 12.1 g. of 2,2,5,5-tetramethyltetrahydrofuran, b.p. 68–70° (160 mm.), n^{25}_{D} 1.4027, and 6.8 g. (26%) of the desired alcohol, b.p. 66.0–66.6° (20 mm.), n^{25}_{D} 1.4427; lit.[23] b.p. 63.5–64° (15 mm.), n^{20}_{D} 1.4438. Confirmation of the assigned structure of the alcohol was obtained from its n.m.r. spectrum. The peak positions, relative areas, and assignments were as follows: 4.70 (0.9) broad triplet ($J = 7.5$ c.p.s.) assigned to C-4 vinyl proton; 5.81 (1.0) single hydroxyl proton; 7.80 (2.2) doublet ($J = 7.5$ c.p.s.) assigned to C-3 protons; 8.27 and 8.37 (6.1) nonequivalent C-5 methyl groups; and 8.82 τ (5.9) C-2 methyl groups.

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A Facile Skeletal Rearrangement. Reidentification of "2,2,4-Trimethylpentane-1,4-diol"[1]

CHARLES F. WILCOX, JR., AND DAVID L. NEALY[2]

Department of Chemistry, Cornell University, Ithaca, New York

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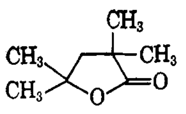
The compounds previously reported to be 2,2,4-trimethylpentane-1,4-diol and the corresponding dibromide are reidentified as 2,5-dimethylhexane-2,5-diol and dibromide, respectively. Synthesis of the authentic 1,4-diol is reported. From the solvolysis of the related 2,2,4-trimethyl-3-penten-1-ol *p*-toluenesulfonate it is concluded that the erroneous structure assignment resulted from an extremely facile skeletal rearrangement proceeding through a cyclopropylcarbinyl cation.

In connection with the identification of products obtained from the dehydration of 2,2,4,4-tetramethylcyclobutane-1,3-diols,[3] 2,2,4-trimethyl-4-valerolactone (**1**) was reduced in 78% yield with lithium aluminum hydride to 2,2,4-trimethylpentane-1,4-diol (**2**). Although the diol was identified rigorously, its melting point differed by 50° from that reported earlier for the same diol by Mossler.[4] The possibility of an unexpected rearrangement in the previously reported preparation was suggested by the extremely facile skeletal rearrangement observed in the solvolysis of the related 2,2,4-trimethyl-3-penten-1-ol *p*-toluenesulfonate. This paper discusses these rearrangements and confirms the suspected earlier misassignment of structure.



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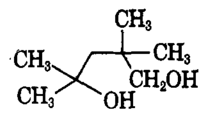

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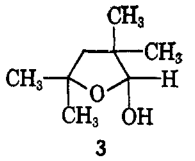

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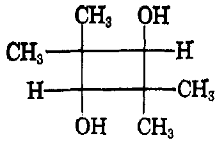

Results and Discussion

Acid dehydration[5] of 2,2,4,4-tetramethylcyclobutane-1,3-diol (**4**) has been reported[3] to give some 3,3,5,5-tet-

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[1] Abstracted from the Ph.D. dissertation submitted by D. L. N. to Cornell University, 1963.

[2] National Science Foundation Predoctoral Fellow, 1959–1963.

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