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.[23] 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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[22] E. L. Jenner, *Org. Syn.*, **40**, 90 (1960).

[23] T. A. Favorskaya and H. P. Ryzhoba, *Zh. Obshch. Khim.*, **26**, 423 (1956).

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

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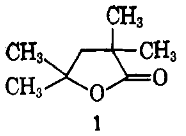
The compounds previously reported to be 2,2,4-trimethylpentane-1,4-diol and the corresponding dibromide are reidentified as 2,5-dimethylhexane-2,5-diol and dibromide, respectively. Synthesis of the authentic 1,4-diol is reported. From the solvolysis of the related 2,2,4-trimethyl-3-penten-1-ol *p*-toluenesulfonate 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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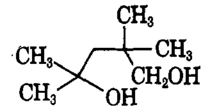
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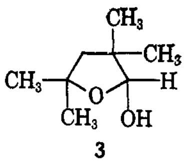
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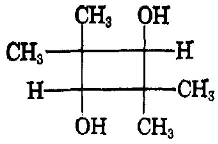

Results and Discussion

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.

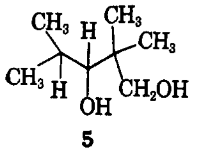
[3] C. F. Wilcox, Jr., and D. L. Nealy, *J. Org. Chem.*, **28**, 3450 (1963).

[4] G. Mossler, *Monatsh.*, **24**, 595 (1903).

[5] R. H. Hasek, R. D. Clark, and J. H. Chaudet, *J. Org. Chem.*, **26**, 3130 (1961).

ramethyltetrahydro-2-furanol (**3**). As part of the structure proof of this cyclic hemiacetal it was oxidized in 58% yield with chromium trioxide–pyridine complex by the method of Sarett[6] to 2,2,4-trimethyl-4-valerolactone (**1**). The lactone was reduced with excess lithium aluminum hydride to form a solid, m.p. 36–37°, in 78% yield. Elemental analysis, the infrared spectrum, and especially the n.m.r. spectrum strongly supported the expected structure, that of 2,2,4-trimethylpentane-1,4-diol (**2**). The n.m.r. peak positions, relative areas, and assignments were as follows: 4.36 (2.0), hydroxyl hydrogens; 6.62 (1.7), C-1 hydrogens; 8.45 (2.2), C-3 hydrogens; 8.70 (5.9), C-4 methyl groups; and 9.00 τ (6.2), C-2 methyl groups. In confirmation of this structure, the diol **2** was converted in 78% yield to the known 2,2,4,4-tetramethyltetrahydrofuran by shaking a pentane solution of **2** with concentrated sulfuric acid for 10 min. at room temperature.

Diol **2** had been reported previously by Mossler[4] to melt at 86°. His synthesis involved treatment of 2,2,4-trimethylpentane-1,3-diol (**5**) with 68% hydrobromic acid at 70–80° for 14 hr. to form a dibromide, m.p. 68°, followed by reaction of the dibromide with excess silver oxide to form a solid diol, m.p. 86°. The suspicion that the first of these reactions led to skeletal rearrangement is supported by Mossler's inability to oxidize his diol and by the fact that "rearranged" dibromide **6** and **7** have been reported[7] to melt at 68° and 86°, respectively. This rearrangement at first seems rather drastic.[8] However, a very simple path for such skeletal change involving the homoallylic bromide **8**, can be envisioned.



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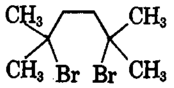

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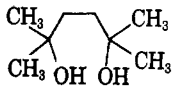

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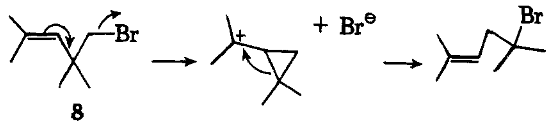

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Analogies for this rearrangement have been reported.[3,9,10] Rogan[10] found that the solvolysis rate of 4-methyl-3-penten-1-ol tosylate (**9**) was 1200 times that of ethyl tosylate, and that one of the solvolysis products was 2-cyclopropylpropene. He concluded that the solvolysis proceeded *via* a nonclassical cyclopropylcarbinyl cation. In an extension of this work, 2,2,4-trimethyl-3-penten-1-ol (**10**) and its tosylate (**11**) have been prepared and solvolyzed to determine the effect of the pair of β-methyl groups on the rate and products of solvolysis. The rate constants, given in Table I, show that the β-methyl groups cause a rate increase of about two powers of ten over Rogan's tosylate (**9**). This is in marked contrast to the effect of β-methyl groups in saturated alkyl tosylates as demonstrated by the comparison of ethyl and neopentyl tosylates.[11] Thus the observed rate acceleration of **11** relative to neopentyl tosylate as a reference compound is 8.1 × 10^6. The additional rate enhancement of **11** over **9** from introduction of a pair of β-methyl groups presumably arises from their stabilizing effect on the three-membered ring of the cyclopropylcarbinyl cation. Similar rate effects of *gem*-dimethyl groups on reactions involving formation of small rings are well known.[12]

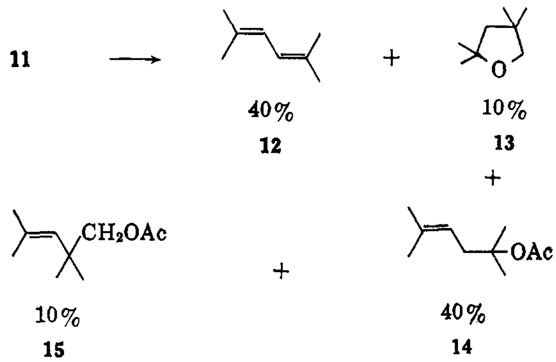
TABLE I

Compound	Temp., °C.	Solvent	k_1, sec.$^{-1}$
2,2,4-Trimethyl-3-pentene-1-ol tosylate (11)	50.00	90% acetone	7.50×10^{-4}
	25.00	AcOH	2.75×10^{-4}
4-Methyl-3-penten-1-ol tosylate (9)	60	AcOH	$1.66 \times 10^{-4\,b}$
	45	AcOH	$3.16 \times 10^{-5\,b}$
Ethyl tosylate	25.00	AcOH	$1.78 \times 10^{-9\,a,c}$
Neopentyl tosylate	25.00	AcOH	$3.41 \times 10^{-11\,a,c}$

[a] Extrapolated from data at other temperatures. [b] Ref. 8. [c] Ref. 11.

Rogan[10] isolated isopropenylcyclopropane from solvolysis of tosylate **9**. The failure to observe dimethylisopropenylcyclopropane in the products from solvolysis of **11** might seem to contradict the proposed extra stability of the cyclopropylcarbinyl intermediate. The different behavior of the two tosylates can be rationalized as a facile opening of the intermediate from **11** to give a stable tertiary carbonium ion compared to a more difficult opening of the intermediate from **9** to give a primary carbonium ion.

The major products of acetolysis of **11** were found to have the rearranged carbon skeleton of **12** and **14**, as shown. Products **14** and **15** were identified as the alcohols, obtained by lithium aluminum hydride reduction of the acetate mixture. All these products were synthesized independently by straightforward routes (see Experimental for details). Thus, the rearrangement postulated for the rationalization of Mossler's results is found to occur even under extremely mild conditions. The two minor products could have arisen from possible contamination of **11** with unconverted alcohol **10**.



Finally, the earlier work[4] was repeated. It was found that treatment of the 1,3-diol **5** with 48% hydrobromic acid at 70–80° for 4 hr. merely effected dehydration and

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[6] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 427 (1953).

[7] S. Pogorshelski, *J. Russ. Chem. Soc.*, **30**, 983 (1898); **35**, 884 (1903).

[8] The observed rearrangement is represented formally by a 1,2 shift of the substituted isobutyl group from C-2 to C-1. This direct shift seems improbable since no product from the competing 1,2 shift of the C-2 methyl groups was found.

[9] J. L. Corbin, H. Hart, and C. R. Wagner, *J. Am. Chem. Soc.*, **84**, 1740 (1962).

[10] J. B. Rogan, *J. Org. Chem.*, **27**, 3910 (1962).

[11] S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

[12] For examples of rate effects, see C. A. Grob and F. A. Jenny, *Tetrahedron Letters*, No. **23**, 25 (1960); C. R. Lindegren and S. Winstein, Abstracts of Papers, 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1953, p. 30M.

ring closure to 2,2,4,4-tetramethyltetrahydrofuran (**13**) without appreciable skeletal rearrangement. However, heating **5** with 60–65% hydrobromic acid for 14 hr. at 70–80° (approximately Mossler's mildest conditions), produced a solid dibromide, m.p. 67.5–68.5°, which was shown by its n.m.r. spectrum to have the rearranged, more symmetrical structure of **6**. Only two peaks were observed, at 7.99 and 8.20 τ with integrated areas in the ratio 1.00:3.00, respectively. This dibromide was hydrolyzed by warm aqueous acetone containing potassium carbonate to 2,5-dimethylhexane-2,5-diol (**7**), m.p. 85.5–86.5°, identified by its n.m.r. spectrum, which consisted of three peaks at 6.94, 8.57, and 8.89 τ with relative areas 1:2:6; and by comparison of its infrared spectrum with that of a sample of **7** prepared by the reaction of methylmagnesium iodide with hexane-2,5-dione.

Experimental[13]

3,3,5,5-Tetramethyltetrahydro-2-furanol. Method A.—Commercial 2,2,4,4-tetramethylcyclobutane-1,3-diol (Eastman), 250 g., was dehydrated by the procedure of Hasek, *et al.*[5] except that the sulfuric acid concentration was maintained at 10–15%. Fractional distillation of the dried organic steam distillate afforded three distinct fractions. The first was 2,2,4-trimethyl-3-pentenal, b.p. 82–85° (100 mm.), 35 g., $n^{25}\mathrm{D}$ 1.4365, as reported.[5] The second, b.p. 110–111° (76 mm.) or 91–92° (32 mm.), 13.5 g., crystallized on standing. An analytical sample was obtained by recrystallization from pentane at −60°, m.p. 53.2–54.0°.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.60; H, 11.18. Found: C, 66.50; H, 11.15.

This solid showed strong hydroxyl absorption in its infrared spectrum. Its n.m.r. spectrum (with benzene as solvent) consisted of two low field peaks at 4.99 and 5.22, four singlets at 8.58, 8.77, 8.86, and 8.99, and a quartet (J = 12 c.p.s.) centered at 8.33 τ, with relative integrated areas 1:1:3:3:3:3:2, respectively. Addition of acetic acid to the benzene solution[14] caused the disappearance of the peak at 5.22 τ, but no change in any of the other peaks, indicating the presence of only one hydroxyl group. This data and the oxidation of the solid described subsequently identify it as 3,3,5,5-tetramethyltetrahydro-2-furanol.

Method B.—A solution of 1.00 g. of 2,2,4-trimethyl-3-pentenal[5] in 20 ml. of 75% acetone–water containing 0.12 *N* p-toluenesulfonic acid was heated for 30 hr. at 100°. The cooled solution was diluted with 75 ml. of ether, extracted twice with 50 ml. of 6 *N* sodium hydroxide solution, dried over magnesium sulfate, and evaporated to a volume of about 3 ml. The residue was separated by g.l.c. on a silicon oil preparative column at 120° into mesityl oxide, the starting aldehyde, and 3,3,5,5-tetramethyltetrahydro-2-furanol, m.p. 54–55°. The two latter products were isolated in 33% and 48% yields, respectively. Infrared spectra of all three products were identical with those of known samples.

2,2,4-Trimethyl-4-valerolactone (**1**).—Chromium trioxide–pyridine complex[6] was prepared by cautious addition of 10.0 g. of chromium trioxide (Mallinkrodt A.R.) to 180 ml. of dry pyridine under a nitrogen atmosphere over a period of 40 min. The resulting suspension was stirred for an additional 30 min. and a solution of 5.0 g. of 3,3,5,5-tetramethyltetrahydro-2-furanol (**3**) in 30 ml. of pyridine was added dropwise over 30 min. The mixture was stirred at room temperature for 3 hr. more, and filtered. The clear filtrate was diluted with 300 ml. of ether, washed with seven 100-ml. portions of 4 *N* hydrochloric acid, dried over magnesium sulfate, and evaporated under aspirator vacuum. The residue, 2.85 g., crystallized on cooling, m.p. 38–40°. Recrystallization from petroleum ether (b.p. 30–60°) at −60° afforded 2.60 g. colorless needles, m.p. 43.0–44.0°.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 68.15; H, 10.00.

This solid exhibited infrared absorption at 1760 cm.$^{-1}$ consistent with a γ-lactone structure. Its n.m.r. spectrum showed three single peaks at 7.99, 8.56, and 8.72 τ with relative areas of 2.1:6.1:5.9, respectively, assigned to the β-methylene group, the pair of γ-methyls, and the pair of α-methyls of **1**. Compound **1** has been reported to melt at 42°.[15]

2,2,4-Trimethylhexane-1,4-diol (**2**).—Reduction of 1.00 g. of lactone **1** was effected with a suspension of lithium aluminum hydride in tetrahydrofuran at room temperature for 3 hr. On hydrolysis, filtration, and evaporation of solvent, 0.82 g. of residue was obtained, which was found to be about 96% pure by g.l.c. on a silicon oil column. A sample collected from this column showed an infrared spectrum (strong hydroxyl absorption) identical with that of the crude product. The collected sample crystallized on cooling, m.p. 36–37°.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.71; H, 12.40. Found: C, 65.36; H, 12.31.

2,2,4,4-Tetramethyltetrahydrofuran (**13**).—A solution of 0.25 g. of diol **2** in 5 ml. of pentane was shaken for 10 min. with 3 ml. of 97% sulfuric acid. After addition of 15 g. of ice and 10 ml. of ether, the organic phase was separated, washed with 10 ml. of 5% sodium hydroxide solution, dried over magnesium sulfate, and evaporated to a volume of 1 ml. The residue was found by g.l.c. analysis on a silicon oil column to consist of only one component in addition to the low boiling solvents. The single product collected was a liquid, $n^{25}\mathrm{D}$ 1.4098, which showed no O—H or C═C absorption in its infrared spectrum. Its n.m.r. spectrum showed four single peaks at 6.64, 8.46, 8.81, and 8.94 τ with relative areas 1:1:3:3, respectively (lit.[16] for **13** $n^{25}\mathrm{D}$ 1.4061; lit.[17] n.m.r. spectrum 6.6, 8.40, 8.77, 8.91 τ; areas, 1:1:3:3).

Further confirmation of the identity of **13** was obtained by its preparation from both diol **5** and 2,2,4-trimethyl-3-penten-1-ol (**10**) as described in this section.

2,2,4-Trimethyl-3-penten-1-ol (**10**).—Twenty grams of 2,2,4-trimethyl-3-pentenal[5] was reduced with 3.0 g. of lithium aluminum hydride in refluxing ether over 3 hr. Hydrolysis, filtration, and distillation of the reaction mixture afforded 17.0 g. (85%) of the alcohol, b.p. 89–90° (60 mm.), $n^{25}\mathrm{D}$ 1.4546. An n.m.r. spectrum of this alcohol showed a multiplet at 5.00 (J = 1.9 c.p.s.), a singlet at 6.60, a singlet at 6.74, a doublet at 8.30 (J = 1.9 c.p.s.), and a singlet at 8.93 τ with relative areas 1:1:2:6:6, respectively. A 3,5-dinitrobenzoate derivative was prepared and recrystallized from 90% ethanol, m.p. 59.5–60.5°. The alcohol was converted into the previously described 2,2,4,4-tetramethyltetrahydrofuran (**13**) on passage at 130° through a g.l.c. column of silicon oil containing traces of acid.

2,2,4-Trimethyl-3-penten-1-ol Tosylate (**11**).—To 5.0 g. of 2,2,4-trimethyl-3-penten-1-ol (**10**) in 50 ml. of pyridine was added 7.0 g. of *p*-toluenesulfonyl chloride. The resulting solution was left at room temperature for 24 hr., cooled to 0°, and poured into 100 ml. of isopentane and 200 ml. of ice–water. After thorough mixing, the organic layer was separated, washed twice with 100 ml. of cold water, twice with 100 ml. of 3 *N* hydrochloric acid, and finally with water. Ammonia gas was bubbled through the solution to remove any unchanged *p*-toluenesulfonyl chloride, but no precipitate was observed. The solution was dried over magnesium sulfate, filtered, evaporated, and then heated at 50° (2 mm.) for 1 hr., leaving 9.0 g. of liquid residue. An infrared spectrum of this liquid showed typical tosylate absorptions at 1600 and 1360, but no hydroxyl absorption in the 3100–3500-cm.$^{-1}$ region.

Determination of Solvolysis Rates.—Mallinkrodt A.R. acetone was refluxed for 8 hr. with potassium permanganate and Drierite and distilled from fresh Drierite. Nine volumes of the center fraction were combined with one volume of distilled water at 25.0° to make 90% (v/v.) acetone–water. Baker "analyzed reagent" acetic acid was dried with the required amount of acetic anhydride, calculated from Karl Fisher titration.[18] Kinetic data for the solvolysis in 90% acetone–water was obtained by the sealed ampoule technique. Aliquots were titrated against 0.0331

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[13] Melting points are corrected. N.m.r. spectra were determined on a Varian A-60 analytical spectrometer from the pure liquids or carbon tetrachloride solutions of solids unless otherwise noted. All spectra used tetramethylsilane as an internal standard.

[14] Addition of acetic acid to an inert solvent has been used to identify hydroxyl hydrogens by n.m.r.; D. E. Applequist and G. F. Fanta, *J. Am. Chem. Soc.*, **82**, 6393 (1960).

[15] A. Franke, *Monatsh.*, **17**, 85 (1896).

[16] F. F. Rust and D. O. Collamer, *J. Am. Chem. Soc.*, **76**, 1055 (1954).

[17] F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).

[18] A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

N sodium methoxide in absolute methanol to a bromthymol blue end point. The acetolysis was run in a stoppered flask containing 0.04 N sodium acetate in acetic acid. Aliquots were transferred to a precooled 50-ml. erlenmeyer flask, cooled in ice, and immediately titrated to a bromphenol blue end point with a solution of 0.0356 N perchloric acid in acetic acid. Both reactions were followed kinetically to 90% completion; they gave excellent first-order plots over this range when the experimental infinities were employed. The observed infinity titer (acetone–water) was 91% of the calculated value.

Acetolysis Products from 2,2,4-Trimethyl-3-penten-1-ol Tosylate (11).—The ester **11** (8.0 g.) was solvolyzed in 90 ml. of 99.8% acetic acid containing 4.0 g. of sodium acetate at 50.0 ± 0.05° for 1 hr. (about 20 half-lives). The solution was diluted with 200 ml. of isopentane, extracted twice with concentrated salt solution, then with water, shaken with solid sodium carbonate, and dried over magnesium sulfate. Distillation through a 20-cm. Vigreux column afforded, in addition to solvent, two distinct fractions, b.p. 42–46° (21 mm.) and b.p. 81–83° (19 mm.). About 1.0 g. of a nonvolatile waxy residue remained in the flask. The low boiling fraction, weighing 0.90 g., was further separated by g.l.c. at 100° on a 5 ft. × 0.5 in. column of 20% SF-96 silicon oil–Chromosorb W into 20% 2,2,4,4-tetramethyltetrahydrofuran (**13**), retention time 4.2 min., and 80% 2,5-dimethyl-2,4-hexadiene (**12**), retention time 6.5 min. Both these compounds were identified by comparison of infrared and n.m.r. spectra with those of authentic samples, obtained as described in this section.

The higher boiling fraction, presumed to contain acetate esters on the basis of strong infrared absorption at 1725 cm.$^{-1}$, was reduced with lithium aluminum hydride in refluxing ether over 20 hr. The usual work-up and evaporation of solvent left 0.95 g. of a mixture of alcohols, which were separated on the same g.l.c. column at 108°. The major component (81%), retention time 5.7 min., n^{25}D 1.4433, was identified as 2,5-dimethyl-3-hexen-2-ol by comparison of its infrared and n.m.r. spectra with those of an authentic sample, obtained as described subsequently. The minor component (19%), retention time 7.7 min., n^{25}D 1.4535, was found to be 2,2,4-trimethyl-4-penten-1-ol (**10**) by comparison with the starting alcohol. It should be noted that both minor products **10** and **13** may have arisen from the presence of **10** as an impurity in the tosylate **11**. That some unchanged **10** was present is suggested by the low (91%) infinity titer from the solvolytic rate measurement.

2,5-Dimethylhexane-2,5-diol (7).—To a solution of methylmagnesium iodide prepared from 30 g. of magnesium, 200 g. of methyl iodide, and 500 ml. of ether was added at 0° an ether solution of 50 g. of 2,5-hexanedione over about 1 hr. After an additional hour at room temperature, the mixture was poured over ice and dilute sulfuric acid. The ether phase was separated, washed with dilute aqueous base, dried over magnesium sulfate, and evaporated. The solid residue was recrystallized from carbon tetrachloride, giving 32 g. (50% yield) of crystals, m.p. 87.5–88°, lit.[19] m.p. 87–88°. The n.m.r. spectrum of this diol consisted of three single peaks at 6.94, 8.57, and 8.89 τ with relative areas 1:2:5, respectively.

2,5-Dimethyl-4-hexen-2-ol.—This alcohol was prepared from diol **7** by acid dehydration according to the method of Favorskaya and Ryzhoba.[20] The crude steam distillate was dried over magnesium sulfate and separated by fractional distillation into two components. The first was 2,2,5,5-tetramethyltetrahydrofuran, b.p. 68–70° (160 mm.), n^{25}D 1.4027, 49%; lit.[20] b.p. 115.5–116.5°, n^{20}D 1.4014. The second was the desired alcohol, b.p. 66.0–66.6° (20 mm.), n^{25}D 1.4427, 26%; lit.[20] b.p. 63.5–64° (15 mm.), n^{25}D 1.4438. Confirmation of the assigned structure 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.

2,5-Dimethyl-2,4-hexadiene (12).—To a solution of 3.1 g. 2,5-dimethyl-4-hexen-2-ol in 20 ml. of dry pyridine was added cautiously, with external cooling, 3.0 ml. of thionyl chloride. The reaction mixture was left at room temperature for 4 hr., poured into 100 ml. of cold water, and extracted twice with 25 ml. of ether. The ether extracts were washed with four 100-ml. portions of 3 N hydrochloric acid, dried over magnesium sulfate, and evaporated to a volume of about 4 ml. About equal quantities of three compounds were isolated by g.l.c. on a 20% silicon oil column at 109°. The desired diene **12** (34%), retention time 4.1 min., n^{25}D 1.4640, m.p. 22–24°, showed infrared absorption at 1620 cm.$^{-1}$ and ultraviolet absorption maximum at 242 mμ (ϵ 25,900), lit.[21] 242 (25,200).

The n.m.r. spectrum of this diene supported the symmetrical structure **12**. Three single peaks were observed at 6.06, 8.27, and 8.33 τ. The low field peak had an area of 1.9 relative to 12.0 for the combined area of the two high field peaks.

The two other components of the product mixture were isolated and tentatively identified. The first (36%), retention time 2.5 min., n^{25}D 1.4324, was assigned the structure of 2,5-dimethyl-1,4-hexadiene on the basis of its n.m.r. spectrum, which consisted of a broad triplet (J = 1.5 c.p.s.) at 4.83, a broad peak or multiplet at 5.32, a doublet (J = 1.5 c.p.s.) at 7.33, a singlet at 8.31, and a singlet at 8.50 τ, with respective relative areas 1:2:2:6:3. The last component (30%), retention time 6.8 min., n^{25}D 1.4450, gave a positive test for chloride on treatment with ethanolic silver nitrate. This compound was assigned the structure of 5-chloro-2,5-dimethyl-2-hexene from its n.m.r. spectrum, which included a broad triplet (J = 7.5 c.p.s.) at 4.71, a doublet (J = 7.5 c.p.s.) at 7.59, and singlets at 8.27, 8.39, and 8.49 τ with relative areas approximating the proportion 1:2:3:3:6.

Reaction of 2,2,4-Trimethylpentane-1,3-diol (5) with Hydrobromic Acid. Method A.—Ten grams of diol was heated at 70–80° with 225 g. 48% hydrobromic acid in a sealed thick-walled glass bomb for 4 hr., then cooled and transferred to a 1-l. separatory funnel containing 300 ml. of cold water and 100 ml. of pentane. The organic phase was separated, dried over magnesium sulfate, and evaporated to a liquid residue (7.4 g.) which was analyzed by g.l.c. on a silicon oil column at 105°. A sample of the major component was collected and shown to be 2,2,4,4-tetramethyltetrahydrofuran, n^{25}D 1.4106, by comparison of its infrared spectrum with that of a sample prepared by cyclization of 2,2,4-trimethyl-3-penten-1-ol (**10**).

Method B.—Ten grams of diol **5** was heated as in method A with 200 g. of 60–65% hydrobromic acid at 70–80° for 15 hr., cooled, and the organic components separated. On cooling the dried pentane solution to −70°, 7.8 g. of crystals were obtained, m.p. 67–68°.

Anal. Calcd. for $C_8H_{16}Br_2$: C, 35.32; H, 5.93; Br, 58.75. Found: C, 34.78; H, 6.05; Br, 57.11.

Hydrolysis of Dibromide 6.—To a solution of 3.0 g. of potassium carbonate in 50 ml. of water and 10 ml. of acetone was added 4.0 g. of **6**. The mixture was heated at 40–50° for 2 hr., cooled, and extracted twice with 50 ml. of ether. The ether extracts were dried over magnesium sulfate and evaporated. The residue was dissolved in 15 ml. of petroleum ether (b.p. 30–60°) and cooled slowly to −50°. Filtration afforded 0.55 g. of crystals, m.p. 85.5–86.5°. This solid was identified as 2,5-dimethylhexane-2,5 diol (**7**) by comparison of its infrared and n.m.r. spectra with those of the sample prepared previously.

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