coverage in the Kolbe reaction both with KTFA and potassium acetate in aqueous acetic acid,[11] is substantially lower than that observable when the electrode is anodically polarized in aqueous sulfuric acid alone.

In conclusion, it may be stated that the presence of water in the solution is not only not necessary for the Kolbe reaction to proceed[9] but in fact leads to significant inhibition effects. This is also borne out by yield studies[4,5] where the best yields of $R_2$ (96% in the case[5] of KTFA giving $C_2F_6$) are usually obtained in a nonaqueous medium, *e.g.*, the anhydrous acid itself containing its own salt as electrolyte.

The above observations may also have a bearing on conclusions which have been made regarding the possible role of carbonium ions[13] in the Kolbe reaction as deduced from the nature of side products. Thus, products such as alcohols ROH or esters which can be formed,[3] might arise, it seems, just as well from steps involving heterogeneous oxidation of adsorbed R· radicals by the Pt surface oxide as from anodic ionisation to form $R^+$ and subsequent rapid reaction with the solvent or electrolyte anions. The entity R·, of course, can arise from decarboxylation of RCOO·[14] produced by discharge of the carboxylate ion.[5]

**Acknowledgment.**—Grateful acknowledgment is made to the National Research Council, Canada, for support of this work. One of us (A. K. V.) acknowledges the award of a Fellowship from the Sprague Electric Co.

(13) E. J. Corey, N. L. Bauld, R. T. Lalonde, J. Casanova, Jr., and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960).
(14) A. Crum-Brown and J. Walker, *Ann.*, **261**, 107 (1891).

## Novel Rearrangement Products of 2,2-Dimethyl-1-(tetrahydro-2-furyl)-1,3-propanediol

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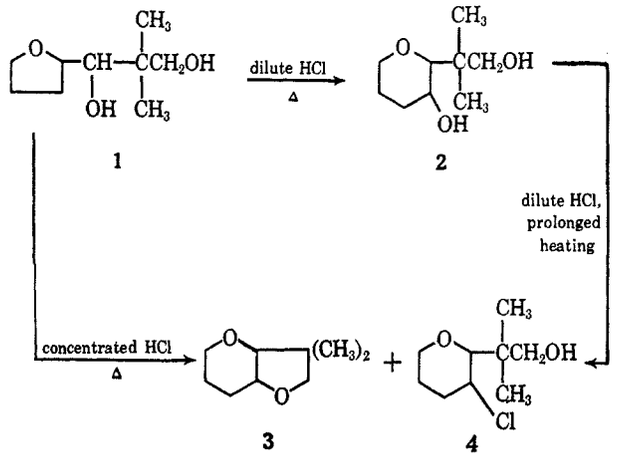
We have found that the furan ring of 2,2-dimethyl-1-(tetrahydro-2-furyl)-1,3-propanediol (**1**) enlarges in the presence of aqueous hydrochloric acid to form three tetrahydropyran derivatives, **2–4**. The relative amount of each compound formed depends upon the acid concentration and the reaction time. (See Scheme I.) This ring enlargement is similar to the isomerization of tetrahydrofurfuryl alcohol to 2,3-dihydropyran.[1]

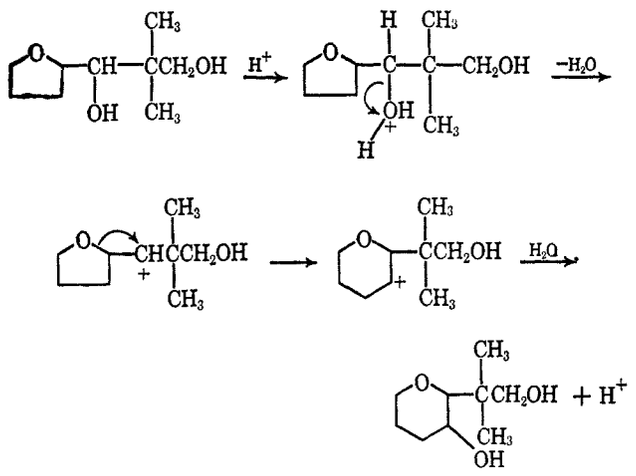
When dilute hydrochloric acid was used, tetrahydro-3-hydroxy-β,β-dimethylpyran-2-ethanol (**2**) was the major product. Concentrated hydrochloric acid or prolonged heating in dilute acid was necessary to form 3-chlorotetrahydro-β,β-dimethylpyran-2-ethanol (**4**) and hexahydro-3,3-dimethylfuro[3,2-*b*]pyran (**3**). When either *p*-toluenesulfonic acid or sulfuric acid was used, the product was mostly hexahydro-3,3-dimethylfuro[3,2-*b*]pyran (**3**). Vapor phase chromatography was used to follow one reaction in which dilute hydrochloric acid was used. Although **2** formed first, it gradually was converted to **3** and **4** on prolonged heating.

SCHEME I




A possible mechanism for this rearrangement is shown in Scheme II below in which the secondary OH group is protonated and water is eliminated to form a carbonium ion.

SCHEME II




Each compound reported except hexahydro-3,3-dimethylfuro[3,2-*b*]pyran (**3**) is a mixture of geometric isomers. No attempt was made to separate each isomer. The structure of each compound was assigned on the basis of nmr data in conjunction with infrared and elemental analyses.

### Experimental Section

**2,2-Dimethyl-1-(tetrahydro-2-furyl)-1,3-propanediol (1).**[2]—A mixture of 2-furaldehyde (96 g, 1 mole) and isobutyraldehyde (144 g, 2 moles) was slowly added with stirring to aqueous 1% sodium hydroxide; the reaction temperature was kept at 10–15°. After the addition of the aldehydes was complete, the mixture was stirred for 1 hr. The heavy oil which separated was extracted with ethyl ether, and the ethereal solution was washed thoroughly with water to remove the sodium hydroxide. Evapo-

(1) R. L. Sawyer and D. W. Andrus, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, pp 276, 277.

(2) The aldol condensation of benzaldehyde with isobutyraldehyde has been described by E. Späth, R. Lorenz, and E. Altman, *Ber.*, **76B**, 513 (1943).

ration of the ether gave 236 g of 6-(2-furyl)-2-isopropyl-5,5-dimethyl-*m*-dioxan-4-ol: nmr spectrum[3] ($CCl_4$), multiplets at 0.9 (methyl groups), 1.8 (CH), 4.0–5.0 [OH, OCH, and –OCHO–], and 6.2 (=CH in ring) and a doublet at 7.2 ppm (OCH in ring). Areas were in the proportions of 12:1:4:2:1. The viscous oil was dissolved in methanol (250 ml) and hydrogenated at 100° and 3000 psi in the presence of alcohol-washed Raney nickel (12 g) until no further hydrogen was absorbed. The catalyst was removed by filtration and the product was distilled to give, after removal of methanol and isobutyl alcohol, 129.5 g (74.4%) of **1**: bp 94–97° (0.3–0.4 mm); $n^{20}D$ 1.4772; infrared absorptions[4] (smear), 3.0 (s) $\mu$ and 9.6 (s) $\mu$; nmr spectrum ($CCl_4$), singlet at 0.90 (methyl groups), and multiplets at 1.89 ($CH_2CH_2$ in ring) and 3.10–4.35 ppm (OH, OCH, and $OCH_2$ groups). Areas were in the proportions of 6:4:8.

**Hexahydro-3,3-dimethylfuro[3.2-*b*]pyran (3).**—A mixture of xylene (150 ml), **1** (174 g, 1 mole), and *p*-toluenesulfonic acid (5 g) was heated at 150–192° for 6 hr, and during this time, water (18 ml) was removed by azeotropic distillation. The crude product was washed with a dilute sodium hydroxide solution and then with water. After the xylene was removed, the product was distilled to give 29.5 g (18.9%) of **3**: bp 101–102° (46 mm); $n^{20}D$ 1.4440; infrared absorptions (smear), 8.87 (m), 9.08 (s), 9.40 (m), and 9.65 (s) $\mu$; nmr spectrum (neat), singlet at 1.0 (methyl groups) and multiplets at 1.1–2.1 ($CH_2CH_2$ in ring) and 2.9–4.0 ppm (OCH and $OCH_2$ groups). Areas were in the proportions of 6:4:6.

*Anal.* Calcd for $C_9H_{16}O_2$: C, 69.3; H, 10.3. Found: C, 69.1; H, 10.5.

**3-Chlorotetrahydro-β,β-dimethylpyran-2-ethanol (4).**—A mixture of **1** (522 g, 3 moles) and concentrated hydrochloric acid (200 g) was refluxed for 16 hr. The organic layer which separated on cooling was washed with saturated sodium bicarbonate solution and then with water until the washings were neutral. The products obtained on distillation were 170 g (36.4%) of **3**, bp 101° (46 mm), and 209 g (36.2%) of **4**: bp 104–106° (1 mm); $n^{20}D$ 1.4751; infrared absorptions (smear), 3.0 (s), 9.65 (s), and 15.45 (m) $\mu$; nmr spectrum ($CCl_4$), triplet at 1.03 (methyl groups), broad peak at 1.85 ($CH_2CH_2$ in ring), singlet at 3.36 (OH group), and a multiplet at 3.48–3.78 ppm (OCH, $OCH_2$, and CHCl groups). Areas were in the proportions of 6:4:1:6.

*Anal.* Calcd for $C_9H_{17}ClO_2$: C, 56.2; H, 8.9; Cl, 18.4. Found: C, 56.5; H, 8.8; Cl, 18.3.

**Tetrahydro-3-hydroxy-β,β-dimethylpyran-2-ethanol (2).**—Aqueous 5.8 *N* hydrochloric acid (217.5 g) and **1** (572 g, 3.29 moles) were refluxed for 55 min, and 37 g of the crude reaction mixture was removed for further study. The remainder was separated into two layers after being neutralized with sodium bicarbonate. Benzene (100 ml) was added and the water layer was saturated with sodium chloride. The aqueous phase was withdrawn and concentrated. Additional organic material separated and was added to the main organic layer. After the water was removed from this layer by azeotropic distillation and a forecut was taken, the crude dry product was distilled to give 367.5 g (67.1%) of **2**, bp 112–119° (1 mm). A 252-g portion of this material was recrystallized from an equal weight of ethyl acetate. The crystals were washed with cold ethyl acetate (250 ml) and dried at 50° (10 mm) in a vacuum oven. The yield was 139 g of an odorless, white solid (pure **2**): mp 64–65°; infrared absorptions (KBr), 3.0 (s) $\mu$ and 9.6 (s) $\mu$; nmr spectrum ($CCl_4$), singlet at 1.06 (methyl groups), broad peak at 1.66 ($CH_2CH_2$ in ring), multiplet at 3.3–4.1 ($OCH_2$ and OCH groups), and a singlet at 4.4 ppm (OH groups). Areas were in the proportions of 6:4:6:2.

*Anal.* Calcd for $C_9H_{18}O_3$: C, 62.5; H, 10.4. Found: C, 61.8; H, 10.8.

**Acknowledgment.**—The authors express their appreciation to V. W. Goodlett of these laboratories for his interpretation of the nmr spectra.

(3) Nmr spectra were recorded on a Varian A-60 instrument at 60 Mc and are reported in parts per million, relative to tetramethylsilane as an internal standard.

(4) Infrared spectra were recorded on a Baird AB-2 instrument.

## A Correction on the Optical Rotations of Propylene Bromohydrin and Propylene Oxide

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In the course of some of our studies we had need for propylene oxide of known optical activity; consequently, we embarked on the synthesis of this compound *via* the published procedures shown in eq 1 and 2.[1–3]

$$CH_3\overset{OH}{\overset{|}{C}}HCH_2OH + HBr \longrightarrow CH_3\overset{OH}{\overset{|}{C}}HCH_2Br \qquad (1)$$

$$CH_3\overset{OH}{\overset{|}{C}}HCH_2Br + OH^- \longrightarrow CH_3\overset{O}{\overset{/\backslash}{C}}H—CH_2 + Br^- + H_2O \qquad (2)$$

It seemed unusual to us that the reaction of hydrogen bromide with *dl*-1,2-propanediol should occur only at the primary carbon without concomitant attack at the secondary carbon. Since we wanted to obtain propylene oxide of the highest optical purity, we had to determine the extent of secondary carbon attack which, when starting with optically active glycol, could lead to formation of racemic 2-bromo-1-propanol, for, indeed, the amount of racemic 2-bromo-1-propanol would in turn be reflected in reduced optical activity of propylene oxide. Consequently, we examined the products from the reaction of *dl*-1,2-propanediol and HBr at several temperatures by glpc and nmr spectroscopy and found that the reaction *does not proceed with exclusive formation of 1-bromo-2-propanol* (**1**), *but rather produces substantial amounts of 2-bromo-1-propanol* (**2**). The results of this examination are shown in the Experimental Section.

$$CH_3\overset{OH}{\overset{|}{C}}HCH_2OH + HBr \longrightarrow \underset{\mathbf{1}}{CH_3\overset{OH}{\overset{|}{C}}HCH_2Br} + \underset{\mathbf{2}}{CH_3\overset{Br}{\overset{|}{C}}HCH_2OH}$$

Thus it seemed to us that the only feasible method for obtaining "pure" optically active propylene oxide when starting with optically active 1,2-propanediol was to separate **1** and **2** (*via* preparative glpc) and then to form propylene oxide from each constitutional isomer.[4] By so doing, we could also determine the configuration and optical purity of **2**. Starting with (+)-(*S*)-propylene glycol and HBr we synthesized (+)-(*S*)-1-bromo-2-propanol (**1**) and (−)-(*R*)-2-bromo-1-propanol (**2**).[5] The results of this experiment are summarized in Scheme I. Since the formation of propylene oxide from **1** does not involve the asymmetric center, it is quite apparent from Scheme I

(1) P. A. Levene and A. Walti, *J. Biol. Chem.*, **68**, 415 (1926).

(2) C. C. Price and M. Osgan, *J. Am. Chem. Soc.*, **78**, 4787 (1956).

(3) N. Shieh and C. C. Price, *J. Org. Chem.*, **24**, 1169 (1959).

(4) Instead of "structural isomer" we are adopting the term "constitutional isomer" as used by K. Mislow. See K. Mislow "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1966, p 50.

(5) The absolute configuration of (+)-(*S*)-propylene glycol is based on the observation that the ethyl ester of (−)-(*R*)-lactic acid is reduced by sodium and ethanol to (−)-(*R*)-propylene glycol: P. A. Levene and H. L. Haller, *J. Biol. Chem.*, **67**, 329 (1926). See also E. Baer and H. O. L. Fischer, *J. Am. Chem. Soc.*, **70**, 609 (1948).