The Synthesis of 3-Hydroxyaldehydes, 3-Hydroxy Acetals, and 3-Hydroxy Ethers from 2-Alkoxyoxetanes[1]

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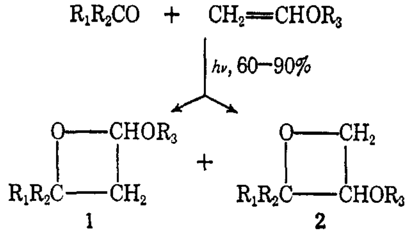
2-Alkoxyoxetanes have been found to react quantitatively under mild conditions with water to give 3-hydroxyaldehydes, with primary, secondary, or tertiary alcohols or phenols to give 3-hydroxy acetals, and with Grignard reagents and lithium aluminum hydride to yield 3-hydroxy ethers. These reactions may be carried out selectively in the presence of the isomeric 3-alkoxyoxetanes which are obtained together with 2-alkoxyoxetanes from the photochemical cycloaddition of carbonyl compounds to vinyl ethers. Hydrolysis of some 3-alkoxyoxetanes to substituted glycerine α-monoethers is also described.

Previously, an efficient photochemical synthesis of 2- and 3-alkoxyoxetanes (**1** and **2**, respectively) from aliphatic and aromatic aldehydes and ketones and vinyl ethers was reported[2] (eq 1). In most cases, the ratio of isomers present in the reaction mixtures could be determined by nuclear magnetic resonance or gas chromatographic analysis. These techniques failed, however, in a number of important cases. It was therefore desirable to develop chemical methods that would permit the determination of the isomer ratios.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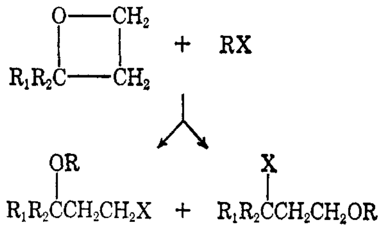
Oxetanes have been shown[3] to react with a large number of compounds such as water, acids, alcohols, etc., to give ring-opened products. Usually, both carbon–oxygen bonds are cleaved in these reactions with subsequent formation of isomeric 3-substituted hydroxy compounds (or derivatives thereof) in moderate to good yields (eq 2). Ring opening of oxetanes generally occurs *via* a carbonium ion mechanism, the rate-determining step being the reaction of the conjugate acid of the oxetane to the final product.[4] Oxetanes with alkoxy groups β to the ring oxygen might therefore be expected to show the same reactivity as the alkyl- and aryl-substituted oxetanes studied earlier. On the other hand, 2-alkoxyoxetanes (four-membered cyclic acetals) would be expected to be much more reactive. A 2-alkoxy substituent will decrease the stability of the conjugate acid with regard to bond breaking since the developing carbonium ion will be stabilized by the alkoxy group. Hopefully, selective reactions of 2-alkoxyoxetanes in the presence of their 3-alkoxy isomers would thus permit an indirect determination of the isomer ratios in the photoproducts. At the same time, selective reactivity would make 2-alkyoxyoxetanes (though minor components in the photomixtures) useful materials for the synthesis of a variety of classes of compounds. Mixtures of the isomeric alkoxyoxetanes from the photoreactions (eq 1) could directly be used for transformation of the 2-alkoxy compounds without prior separation, and isolation of the reaction products from the unreacted 3-alkoxyoxetanes often would be quite simple. These expectations have indeed been found to be fulfilled by experimental evidence and selective transformations of 2-alkoxyoxetanes are described in this paper.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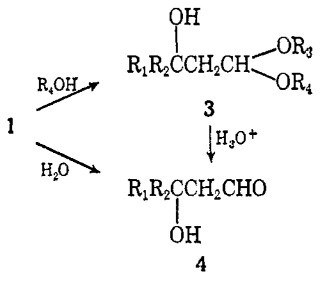
Alcohols and Phenols.—2-Alkoxyoxetanes react readily with primary, secondary or tertiary alcohols upon heating to give acetals of substituted β-hydroxypropionaldehydes (eq 3). Reaction with phenols takes place without heating. By using an alcohol with an alkyl group R_4 different from that present in the alkoxy group OR_3 of the oxetane, mixed acetals can be prepared. Reaction of **1** ($R_1 = R_2 = CH_3$, $R_3 = C_2H_5$) with n-butyl alcohol or of **1** ($R_1 = R_2 = CH_3$, $R_3 = n\text{-}C_4H_9$) with ethanol gives the same mixed acetal. Mixed acetals are the only products, since exchange of alcohol groups does not occur without an acidic catalyst. 3-Alkoxyoxetanes are completely stable under these conditions. Mixtures of 2- and 3-alkoxyoxetanes from the photochemical reactions were therefore used directly in the alcoholysis. The boiling points of the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[1] S. H. Schroeter and C. M. Orlando, Jr., presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstracts, ORGN 15.

[2] S. H. Schroeter and C. M. Orlando, Jr., *J. Org. Chem.*, **34**, 1181 (1969).

[3] For pertinent literature, see S. Searles, Jr., in "Heterocyclic Compounds," A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1964, p 983, and G. Dittus in Houben-Weyl's, "Methoden der organischen Chemie," Vol. VI, 4th ed Georg Thieme Verlag, Stuttgart, 1965, pp 508–515

[4] (a) F. A. Long, J. G. Pritchard, and F. E. Stafford, *J. Amer. Chem. Soc.*, **79**, 2362 (1957); (b) J. G. Pritchard and F. A. Long, *ibid.*, **80**, 4162 (1958).

TABLE I.—ACETALS $R_1R_2C(OH)CH_2CH(OR_3)(OR_4)$ FROM THE ALCOHOLYSIS OF 2-ALKOXYOXETANES **1**[a]

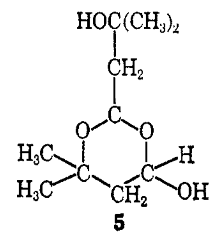
No.	R₁	R₂	R₃	R₄	Bp, °C (mm)	$n^{20}D$	Yield after distn, %	Formula	Calcd Mol wt	Calcd % C	Calcd % H	Found Mol wt	Found % C	Found % H
1	CH_3	CH_3	C_2H_5	C_2H_5	72 (7)	1.4195[b]	96	$C_9H_{20}O_3$	176.25	61.33	11.44	180	61.35	11.65
2	CH_3	CH_3	n-C_4H_9	n-C_4H_9	61 (0.05)	1.4305	82	$C_{13}H_{28}O_3$	232.35	67.19	12.15	240	67.5	12.2
3	CH_3	CH_3	i-C_4H_9	i-C_4H_9	60 (0.05)	1.4774	97	$C_{13}H_{28}O_3$	232.35	67.19	12.15	230	67.27	11.93
4	H	C_2H_5	C_2H_5	C_2H_5	42 (0.05)	1.4242[c]	98	$C_9H_{20}O_3$	176.25	61.33	11.44	180	61.12	11.41
5	$(CH_2)_5$		C_2H_5	C_2H_5	56.5 (0.05)	1.4522	96	$C_{12}H_{24}O_3$	216.31	66.63	11.18	210	66.8	11.3
6	H	C_6H_5	C_2H_5	C_2H_5	86 (0.04)	1.4934	97	$C_{13}H_{20}O_3$	224.29	69.91	8.99	226	69.79	9.10
7	CH_3	CH_3	C_2H_5	n-C_4H_9	53 (0.2)	1.4257[d]	87	$C_{11}H_{24}O_3$	204.30	64.66	11.84	206	64.79	11.92
	CH_3	CH_3	C_2H_5	n-C_4H_9	51 (0.1)	1.4257[e]	71	$C_{11}H_{24}O_3$	204.30	64.66	11.84	196	64.42	11.62
8	CH_3	CH_3	C_2H_5	t-C_4H_9	41 (0.1)	1.4245	87	$C_{11}H_{24}O_3$	204.30	64.66	11.84	204	64.71	11.84
9	CH_3	CH_3	C_2H_5	C_6H_5	97 (0.3)	1.4546	75	$C_{13}H_{20}O_3$	224.29	69.61	8.99	228	69.85	9.17
10	C_6H_5	C_6H_5	C_2H_5	C_2H_5	135 (0.5)		90	$C_{19}H_{24}O_3$	300.38	75.97	8.05	299	76.27	7.84

[a] Purity of acetals was generally greater than 99%, as indicated by vpc and nmr analysis. All compounds had spectral data consistent with the structures given. [b] Prepared earlier [N. L. Wendler and H. L. Slates, *J. Amer. Chem. Soc.*, **72,** 5341 (1950)], but not characterized. [c] Lit. bp 88–90° (8–9 mm), $n^{18}D$ 1.4262 [L. A. Yanovskaya, V. F. Kucherov, and B. G. Kovalev, *Izv. Akad. Nauk SSSR, Ser. Kim.*, 674 (1962); *Chem. Abstr.*, **57,** 16379*c* (1962)]. [d] From 4,4-dimethyl-2-ethoxyoxetane. [e] From 4,4-dimethyl-2-n-butoxyoxetane.

acetals differ markedly from those of the alkoxyoxetanes so that a clean and almost quantitative separation is possible. Results are listed in Table I. Most of the compounds have hitherto been unknown, only a few have been prepared, generally by more difficult routes. 3-Hydroxy acetals can be converted either into the corresponding β-hydroxy[5,6] or α,β-unsaturated[6-8] carbonyl compounds by known methods. The reaction sequence expressed in eq 1 and 3 therefore represents a new synthesis of such aldehydes.

β-Hydroxycarbonyl compounds such as **4** formally represent aldol condensation products of carbonyl compounds R_1R_2CO with acetaldehyde. However, aldol condensation often does not lead to the desired products because of self-condensation of the more reactive carbonyl compounds.[9] Only recently has a modified aldol condensation been developed[6,10] which utilizes metalated Schiff bases of the aldehydes and ketones. It was found that this condensation does not take place with more substituted acetaldehydes. The Schiff base from cyclohexylamine and α,α-diethylacetaldehyde, for example, did not react with benzophenone. No such limitations have yet been found during preparation and alcoholysis of more highly substituted alkoxyoxetanes.[11]

Water.—β-Hydroxyaldehydes can directly be prepared from 2-alkoxyoxetanes by reaction with water (eq 3). Ring opening occurs exothermally upon mixing the reagents at room temperature. The known[7] 3-methyl-3-hydroxybutyraldehyde, **4** ($R_1 = R_2 = CH_3$), was thus obtained from 4,4-dimethyl-2-alkoxyoxetanes. It was isolated as its crystalline dimer which had spectral data consistent with the proposed[7] 1,3-dioxane structure **5**. Pure 3-alkoxyoxetanes do not react with water, even at reflux temperature. It was found, however, that prolonged contact of mixtures of 2- and 3-alkoxyoxetanes with water eventually leads to ring opening of the 3 isomers as well, probably through the catalytic effect of traces of acid formed by autoxidation of the aldehydes. Ring opening of 3-alkoxyoxetanes occurs readily in the presence of dilute acids in the cold or upon treatment with dilute ammonium chloride solution at reflux temperature to give glycerine monoethers in 50–70% yield. Some of the ethers prepared are listed in Table II. The modest yields observed may be due to the fact that oxetanes also undergo acid-



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[5] M. J. van Dam, *Rec. Trav. Chim. Pays-Bas*, **81,** 435 (1962).

[6] G. Wittig and H. Reiff, *Angew. Chem.*, **80,** 8 (1968).

[7] F. G. Fischer, *Chem. Ber.*, **76,** 734 (1943).

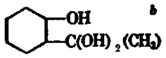
[8] See Table I, footnote *b*.

[9] Houben-Weyl, "Methoden der organischen Chemie," 4th ed, Georg Thieme Verlag, Stuttgart 1954, Vol. VII, 1, p 76.

[10] (a) G. Wittig, W. Stilz, and H. Pommer, French Patent 1,391,323, (March 5, 1965); *Chem. Abstr.*, **63,** P1739c (1965); (b) G. Wittig and H. D Frommeld, *Chem. Ber.* **97,** 3541 (1964); (c) G. Wittig and P. Suchanek, *Tetrahedron Suppl.*, **8,** 347 (1966).

[11] S. H. Schroeter, unpublished data.

TABLE II.—SUBSTITUTED GLYCERINE α-MONOETHERS $[R_1R_2C(OH)CH(OR_3)CH_2OH]$ FROM THE HYDROLYSIS OF 3-ALKOXYOXETANES 2

							Calcd			Found		
No.	R_1	R_2	R_3	Mp or bp, °C (mm)	Yield, %	Formula	Mol wt	% C	%H	Mol wt	% C	% H
1	CH_3	CH_3	C_2H_5	54 (0.4)	70	$C_7H_{16}O_3$	148.20	56.73	10.88	157	56.88	10.91
2	CH_3	CH_3	n-C_4H_9	80 (0.6)	60	$C_9H_{20}O_3$	176.25	61.33	11.44	180	61.33	11.41
3	CH_3	CH_3	i-C_4H_9	60 (0.6)	55	$C_9H_{20}O_3$	176.25	61.33	11.44	179	61.15	11.60
4	C_6H_5	H	C_2H_5	135 (0.2)[a]	67	$C_{11}H_{16}O_3$	196.24	67.32	8.22	194	67.38	8.27
5	 OH C(OH)₂(CH₃) [b]			74–75		$C_8H_{16}O_3$	160.21	59.98	10.07	166	60.12	10.18

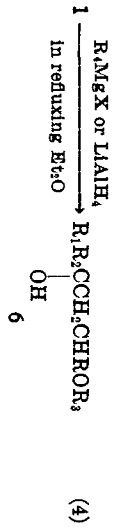
[a] Mixture of diastereoisomers; nmr showed two triplets in a ratio of 1:1 at τ 8.98 and 9.09. [b] Isolated by preparative vpc; all other compounds isolated by spinning-band distillation; purity generally greater than 98% *via* vpc.

TABLE III.—3-HYDROXY ETHERS $[R_1R_2C(OH)CH_2CHR_4OR_3]$ FROM THE REACTION OF 2-ALKOXYOXETHANES 1 WITH GRIGNARD REAGENTS R_4MgX 1–4 AND WITH $LiAlH_4$ 5–8

	3-Hydroxy ether							Calcd			Found		
No.	R_1	R_2	R_3	R_4	Bp, °C (mm)	$n^{20}D$	Formula	Mol wt	% C	% H	Mol wt	% C	% H
1	CH_3	CH_3	n-C_4H_9	CH_3	75 (5)	1.4218	$C_{10}H_{22}O_2$	174.28	68.91	12.72	177	68.75	12.85
2	$(CH_2)_5$		C_2H_5	CH_3	76 (2.2)	1.4526	$C_{11}H_{22}O_2$	186.29	70.92	11.90	190	70.75	11.77
3	C_6H_5	H	C_2H_5	CH_3	80 (0.1)	1.5000	$C_{12}H_{18}O_2$	194.26	74.19	9.34	193	74.38	9.37
4	CH_3	CH_3	C_2H_5	C_6H_5	57 (0.05)	1.4900	$C_{13}H_{20}O_2$	208.92	74.96	9.68	213	75.15	9.74
5	CH_3	CH_3	C_2H_5	H	74.5 (19)	1.4172	$C_7H_{16}O_2$	132.20	63.59	12.20	139	63.44	12.40
6	CH_3	CH_3	n-C_4H_9	H	60 (2.8)	1.4243	$C_9H_{20}O_2$	160.25	67.45	12.58	165	67.32	12.33
7	$(CH_2)_5$		C_2H_5	H	52 (0.2)	1.4588	$C_{10}H_{20}O_2$	168.28	71.37	11.98	169	69.91	11.59
8	C_6H_5	H	C_2H_5	H	76 (0.2)	1.5072	$C_{11}H_{16}O_2$	180.24	73.30	8.95	178	73.23	9.07

catalyzed ring cleavage to carbonyl compounds and olefins.[12]

Grignard Reagents.—When a mixture of 2- and 3-alkoxyoxetanes is added to excess Grignard reagent, the 2-alkoxy isomer reacts exothermally to give, after hydrolysis, 3-hydroxy ethers **6** (eq 4). Vpc analysis



$$1 \xrightarrow[\text{in refluxing } Et_2O]{R_4MgX \text{ or } LiAlH_4} \underset{\substack{| \\ OH}}{R_1R_2C}CH_2CHROR_3 \qquad (4)$$

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shows that conversion of the 2-alkoxy isomers is quantitative after 15 min of refluxing in diethyl ether, while 3-alkoxyoxetanes remain unchanged even after prolonged refluxing. The yield of isolated hydroxy ethers depends solely on the skill with which the ethers are separated from the unreacted 3-alkoxyoxetanes. In the examples studied (Table III, entries 1–4), separation was essentially quantitative in cases where $R_3 > CH_3$ and about 60–80% where $R_3 = CH_3$. Alkyl- and aryl-substituted oxetanes have been found to undergo ring opening with Grignard reagents in moderate yields only upon prolonged treatment at higher temperatures, *e.g.*, in refluxing benzene.[13]

Lithium Aluminum Hydride.—2-Alkoxyoxetanes react selectively when a mixture of 2- and 3-alkoxyoxetanes is treated with excess lithium aluminum hydride in refluxing diethyl ether. Sodium and potassium borohydride proved to be ineffective. The 3-hydroxy ethers prepared are listed in Table III, entries 5–8. Reductive ring opening of the 2-alkoxyoxetanes by lithium aluminum hydride in diethyl ether usually required longer refluxing than did the opening with Grignard reagents. Complexing of the oxetane oxygen with the metal apparently plays an important role. Searles[13a] reported that oxetane itself forms a complex with magnesium bromide, from which 3-bromopropanol-1 is isolated upon hydrolysis. Alkyl- and aryl-substituted oxetanes have been found to react with lithium aluminum hydride only at higher temperatures.[14] With some oxetanes a detectable reaction did not take place even at 140°.[2] However, reduction of oxetanes can be carried out in refluxing diethyl ether with the stronger complexing reagent "mixed hydride."[15]

Experimental Section

Mixtures of 2- and 3-alkoxyoxetanes were prepared as previously reported.[2] Gas chromatographic analyses were performed on a 3-ft Apiezon column on a dual column, temperature-programmed F & M 5750 research chromatograph. Nmr spectra were recorded on a Varian A-60, and ir spectra on a Perkin-Elmer Model 337 spectrometer. Elemental analysis and molecular weight determinations were performed by Galbraith Microanalytical Laboratories. The following examples illustrate the preparation of the compounds listed in Tables I–III.

3-Methyl-3-hydroxybutyraldehyde Diethyl Acetal.—A 60-g sample of a mixture consisting of 24% 4,4-dimethyl-2-ethoxyoxetane and 76% 2,2-dimethyl-3-ethoxyoxetane was refluxed in

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[12] G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4327 (1954).

[13] (a) S. Searles, *ibid.*, **73**, 124 (1951); (b) T. Cuvigny and H. Normant, *C. R. Acad. Sci., Paris*, **254**, 316 (1962).

[14] S. Searles, K. A. Pollart, and E. F. Lutz, *J. Amer. Chem. Soc.*, **79**, 948 (1957).

[15] C. Schaal and J. Seyden-Penne, *C. R. Acad. Sci., Paris, C.*, **266**, (3), 217 (1968).

250 ml of absolute ethanol for 24 hr. Vpc analysis showed that all 2-alkoxyoxetane had been converted into a compound of higher retention time (31%) whereas the 3-alkoxy isomer had remained unchanged. The ethanol was removed through a spinning-band column at 100-mm pressure and the residue fractionated to give two major fractions—30.0 g (84%) of 2,2-dimethyl-3-ethoxyoxetane [bp 65° (60 mm); n^{20}D 1.4102] and 19.08 g (97.5% yield) of the acetal [bp 72° (7 mm); n^{20}D 1.4195; ir (CCl_4, cm^{-1}) 3530 vs, 1125 vs, 1057 vs; nmr (neat, τ) 5.25 (t, 1), *ca.* 6.45 (m, 5, OCH_2, OH), 8.22 (d, 2), 8.80 (s), and 8.82 (t, 12)]. See Table I, entry 1, for analysis. No acetal was obtained when the mixture of oxetanes was refluxed in ethanol containing small amounts of potassium *t*-butoxide.

Hydrolysis.—A 9.0-g sample of the acetal was treated with 40 ml of dilute hydrochloric acid (1:100). The mixture which became homogeneous shortly after mixing was allowed to stand at room temperature for 1 hr, neutralized with potassium carbonate and evaporated *in vacuo*. The residue was treated with ether to yield 3.41 g (69%) of 3-methyl-3-hydroxybutyraldehyde, identical with the compound the preparation of which is described below.

3-Methyl-3-hydroxybutyraldehyde Ethyl Phenyl Acetal.—A solution of 20 g of phenol and 65 g of a mixture consisting of 20% 4,4-dimethyl-2-ethoxyoxetane and 80% 2,2-dimethyl-3-ethoxyoxetane in 250 ml of ether was refluxed for 8 hr. Vpc analysis now showed a mixture consisting of 75% unreacted 3 isomer and 25% of a compound of higher retention time. The solution was extracted several times with 10% sodium hydroxide solution and brine and dried ($MgSO_4$). Distillation through a spinning-band column afforded 54.3 g of material, including 30.0 g of the 3-ethoxyoxetane and 17.16 g (75%) of the acetal: bp 97° (0.3 mm); n^{20}D 1.4546; ir (CCl_4) 3615 s, 3550 vs, 3040 m, 3030 m, 1595 vs, 1490 vs, 1375, 1215, 1190–1170, 1140, 1025, 1000, 965, 960 (all vs); nmr (CCl_4, τ) 2.9 (m, 5), 4.53 (t, 1, $J = \sim 6$ cps), 6.46 (q, 3, $J = \sim 7$ cps), 8.05 (d, 2, $J = \sim 6$ cps), 8.78 (s) and 8.89 (t, 9, $J = \sim 7$ cps). See Table I, entry 9, for analysis.

Hydrolysis of 4,4-Dimethyl-2-ethoxyoxetane.—A 60-g sample of a mixture containing 20% 4,4-dimethyl-2-ethoxyoxetane and 80% 2,2-dimethyl-3-ethoxyoxetane was shaken with 200 ml of water for 15 min. The mixture warmed considerably during this period. The organic phase was taken up with little ether. Vpc analysis indicated that most of the 2-ethoxyoxetane had reacted and was present in the aqueous layer. This was evaporated *in vacuo* to afford, after distillation, 4.0 g of 3-methyl-3-hydroxybutyraldehyde, bp *ca.* 50° (5 mm), which crystallized upon standing. The organic layer was distilled through a short Vigreux column to afford the unreacted 3-alkoxyoxetane and another 0.6 g of aldehyde (4.6 g, 55%) which also crystallized. When the mixture of alkoxyoxetanes and water was shaken for a longer period, or heated, the 3-alkoxy isomer also underwent ring opening and a mixture of 3-methyl-3-hydroxybutyraldehyde and 3-methyl-2-ethoxy-butane-1,3-diol was obtained. The dimer of 3-methyl-3-hydroxybutyraldehyde had mp 81° [from ether–petroleum ether (bp 30–60°)] (lit.[5] mp 91°); ir (CCl_4, cm^{-1}) no carbonyl, 3580 m and 3480 vs, br (OH), 1368, 1150, 1125, 1105 and 1003, all vs; nmr (CCl_4, τ) 4.90 (t, 2), 5.3 (s, OH, 2), 8.03–8.43 (m), 8.50 (s), 8.67 (s) and 8.72 (s), total of 16 H.

Hydrolysis of 2,2-Dimethyl-3-ethoxyoxetane. A.—A 10.0-g sample of the oxetane was shaken with 60 ml of dilute hydrochloric acid (1:100); the mixture warmed and became homogeneous. The solution was allowed to stand at room temperature for 4 hr, was made slightly alkaline with sodium carbonate and evaporated *in vacuo*. The residue was taken up in ether which was dried ($MgSO_4$) and evaporated, to afford, after distillation, 7.91 g (70%) of 3-methyl-2-ethoxy-butane-1,3-diol, which was shown to be 95% pure by vpc.

B.—A mixture of 10 g of the oxetane, 20 ml of water and four drops of acetic acid was shaken at room temperature but no reaction occurred. The mixture was then refluxed for 1.5 hr and the homogeneous solution was worked up as above to afford 4.0 g (35%) of pure diol (*via* vpc).

C.—A 15-g sample of oxetane, 60 ml of water and 3 g of ammonium chloride were refluxed for 12 hr. Evaporation of the aqueous layer and distillation gave 9.6 g (57%) of diol. The combined products from A, B and C were redistilled through a spinning-band column to afford a diol of 99% purity as indicated by vpc. See Table II, entry 1, for analysis. The other compounds listed in Table II were prepared either by method B or C.

2-Methyl-4-*n*-butoxy-2-butanol.—A solution of 10 g of 4,4-dimethyl-2-*n*-butoxyoxetane in 50 ml of ether was slowly added to excess methylmagnesium iodide (prepared from 17.7 g of methyl iodide and 3.0 g of magnesium in 120 ml of ether) at such a rate that the ether solution was kept at gentle reflux. It was then refluxed for an additional 30 min, cooled, and decomposed with ice water and dilute hydrochloric acid. The aqueous layer was twice extracted with ether and the combined ethereal layers were shaken with sodium bicarbonate solution and brine and dried ($MgSO_4$). Distillation afforded 9.07 g (83%) of 2-methyl-4-*n*-butoxy-2-butanol: bp 75° (5 mm); n^{20}D 1.4218; vpc analysis showed only one peak; ir (CCl_4, cm^{-1}) 1180, 1152, 1128, 1082 (all vs); nmr (CCl_4, τ) *ca.* 6.5 (m, 2), 8.3–9.3 (m, 9), with 8.82 (s) and 8.92 (d, $J = 2$ cps). See Table III, entry 1, for analysis. The isomeric 2,2-dimethyl-3-*n*-butoxyoxetane did not react under these conditions.

1-Ethoxy-1-phenyl-2-methyl-2-butanol.—A 60-g sample of a mixture consisting of 28% 4,4-dimethyl-2-ethoxyoxetane and 72% 2,2-dimethyl-3-ethoxyoxetane in 150 ml of ethyl ether was added to excess phenylmagnesium bromide (prepared from 5.0 g magnesium and 32.0 g bromobenzene in 220 ml of ether) and the resulting mixture was refluxed for 30 min, cooled and decomposed with ice and dilute hydrochloric acid. The ethereal layer was extracted with sodium bicarbonate solution and brine and dried ($MgSO_4$). Vpc analysis of the ethereal solution showed a mixture consisting of 65% of the unreacted 3-ethoxyoxetane and 35% of a compound of higher retention time. Distillation afforded 30.2 g of 2,2-dimethyl-3-ethoxyoxetane, bp 69° (66 mm), and 22.6 g (84%) of 1-ethoxy-1-phenyl-2-methyl-2-butanol: bp 57° (0.05 mm), n^{20}D 1.4900; ir (CCl_4, cm^{-1}) 3610 w, 3510 vs, 1600 w, 1495 s, 1115 vs, 1085 vs, 795 vs; nmr (CCl_4, τ) 2.75 (s, 5), 5.30, 5.35, 5.48, 5.53 (all s, 1, X part of ABX), 6.22 (s, 1, OH), 6.67 (q, 2, $J = \sim 7$ cps), 7.78, 7.97, 8.03, 8.19, 8.32, 8.37, 8.55, 8.61 (all s, 9, AB part) 8.70 (s), 8.82 (s), 8.87 (t, $J = \sim 7$ cps). See Table III, entry 4, for analysis.

2-Methyl-4-*n*-butoxy-2-butanol.—A solution of 10 g of 4,4-dimethyl-2-*n*-butoxyoxetane in 40 ml of dry ether was added to 2.0 g of lithium aluminum hydride in 100 ml of diethyl ether and the resulting mixture was gently refluxed for 5 hr. Excess hydride was destroyed by acetone, methanol, and water and the ethereal solution was dried ($MgSO_4$). Vacuum distillation afforded 8.0 g (80%) of 2-methyl-4-*n*-butoxy-2-butanol [bp 60° (2.8 mm), n^{20}D 1.4243], which was purified from traces of higher and lower boiling materials by spinning-band distillation: ir (CCl_4, cm^{-1}) 3520 vs, 1105 vs; nmr (CCl_4, τ) 6.42 (t, $J = \sim 6$ cps), 6.59 (t), 6.80 (s, OH) and 8.32 (t, $J = \sim 6.5$ cps), 8.50 (m), 8.83 (s), 9.07 (m) of relative areas 1:3. Under the same conditions 2,2-dimethyl-3-*n*-butoxyoxetane was not reduced. See Table III, entry 6, for analysis.

Registry No.—Table I—1, 19768-99-1; 2, 19769-00-7; 3, 18267-29-3; 4, 18267-30-6; 5, 18267-39-5; 6, 18267-32-8; 7, 19769-05-2; 8, 19769-06-3; 9, 19769-07-4; 10, 18267-34-0. Table II—1, 19769-09-6; 2, 19769-10-9; 3, 19769-11-0; 4, 19769-12-1; 5, 19769-13-2. Table III—1, 19769-14-3; 2, 19769-15-4; 3, 19769-16-5; 4, 19769-17-6; 5, 19769-18-7; 6, 19769-19-8; 7, 19769-20-1; 8, 18776-18-6.