under reduced pressure. The resulting semicrystalline residue was partially soluble in dry hexane. Cooling of the hexane gave 150 mg (39%) of white crystals: mp 65–68°; ν (CCl_4) 1770 (shoulder), 1760, 1590, 1565 cm^{-1}; nmr (CCl_4) τ 1.97 (m), 2.37 (m), 4.53 (s), 6.70 (s), areas 2:3:1:2.

Anal. Calcd for $C_{11}H_8O_3$: C, 70.21; H, 4.29. Found: C, 70.13; H, 4.34.

The 1-Ethoxyvinyl Enol Ether of IIa, IX.—A solution of 84 mg (0.001 mol) of IIa, 105 mg (0.0013 mol) of ethoxyacetylene, and 5 mg of mercuric acetate in 10 ml of methylene chloride was allowed to stand at room temperature for 5 hr. An infrared spectrum of the solution exhibited absorption at 1760, 1672, and 1578 cm^{-1}. In the nmr spectrum of the solution there is a vinyl ring proton peak at τ 5.03 (s) and ring methylene protons at 6.60 (s); the two terminal vinyl protons are superimposed on the methylene resonance of the ethoxy group at about τ 6.1. When the solvent was removed from the solution, the residue reacted violently with water to give IIa and ethyl acetate.

3-Acetoxy-3-chlorocyclobutanone (X).—A solution of 1.0 g of IIa in 25 ml of acetyl chloride was allowed to stand at room temperature for 2 hr. The excess acetyl chloride was removed under reduced pressure and the residue was distilled *in vacuo*, giving 1.36 g (73%) of X: bp 51–52° (17 mm); ν (CCl_4) 1805, 1785 cm^{-1}; nmr (CCl_4) τ 6.24 (s), 7.86 (s), areas 4:3.

A sample stored at −15° in a sealed tube decomposed to a 50:50 mixture of X and VIIIa after 2 weeks. A sample distilled at aspirator vacuum gave a distillate which was 87% VIIIa. Treatment of 2 drops of X with alcoholic silver nitrate gave an immediate precipitate of silver chloride. When X was treated with sodium iodide in acetone, sodium chloride precipitated upon warming.

When hydrogen chloride was bubbled through a solution of VIIIa in dry benzene, large quantities of X could be detected in the product by infrared and nmr spectroscopy.

Registry No.—Ia, 4683-54-9; Ib, 4313-48-8; IIa, 15506-53-3; IIb, 3183-44-6; III, 38425-45-5; IV, 10576-21-3; V, 38425-47-7; VI, 38425-48-8; VIIa, 38425-49-9; VIIb, 38425-50-2; VIIc, 38425-51-3; VIIIa, 38425-52-4; VIIIb, 38425-53-5; X, 38425-54-6; ketene, 463-51-4; ethoxyacetylene, 927-80-0; aniline, 62-53-3; β-ethoxycrotonic acid anilide, 38425-55-7; isobutyryl chloride, 79-30-1; 2-bromoethoxy-4,4-dimethyl-2-cyclobutenone, 38425-56-8; cyclopentanecarboxylic acid chloride, 4524-93-0; diazomethane, 334-88-3; 3-methoxy-4,4-dimethyl-2-cyclobutenone, 15517-68-7; phenyl bromide, 108-86-1; butyl bromide, 109-65-9; 3,3-dimethoxycyclobutanone, 38425-58-0; pyrrolidine, 123-75-1; 1-ethoxyvinyl benzoate, 38425-59-1.

Base-Induced Cyclizations of Alkyl-Substituted Propargyloxyethanols[1]

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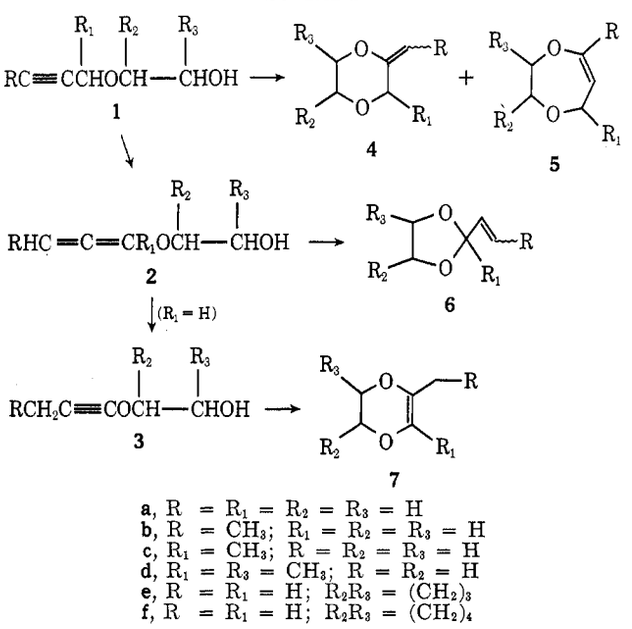
Cyclization reactions of alkyl-substituted propargyloxyethanols **1a–1f** induced by potassium hydroxide in water, dimethyl sulfoxide (DMSO), and *tert*-butyl alcohol were studied. Products obtained included the corresponding 2-methylene-1,4-dioxanes, 3,6-dioxacycloheptenes, 2-vinyl-1,3-dioxolanes, and 2-methyl-1,4-dioxenes. The mechanism proposed to account for base-induced cyclizations of propargyloxyethanol (ref 2) required modification to include two alternative pathways to the 2-methyl-1,4-dioxenes: cyclization of the allenyloxyethanol formed by prototropic rearrangement of the propargyloxyethanol, and, in DMSO only, base-induced rearrangement of the corresponding 2-methylene-1,4-dioxane.

The course of hydroxide-induced cyclization of propargyloxyethanol (**1a**) is strikingly dependent on reaction conditions.[2] In water, the main products are 2-methylene-1,4-dioxane (**4a**) and 3,6-dioxacycloheptene (**5a**); in the aprotic solvents decalin, dimethyl sulfoxide (DMSO), and triglyme, the main products are 2-vinyl-1,3-dioxolane (**6a**) and 2-methyl-1,4-dioxene (**7a**). A mechanism (Scheme I) that accounted for the dependence of product composition on solvent was proposed for the formation of **4a–7a**.[2] Formation of **4a** and **5a** was explained as occurring by intramolecular nucleophilic addition of alkoxide to the internal and terminal acetylenic carbons of **1a**, and the main pathways to **6a** and **7a**, respectively, were pictured as cyclizations of allenyloxyethanol (**2a**) and 1-propynyloxyethanol (**3a**), the products of successive prototropic rearrangements of **1a**.

Faure and Descotes,[3] who cyclized **1a** and six alkyl- and aryl-substituted propargyloxyethanols by treatment with potassium hydroxide in the diol corresponding to the substituted propargyloxyethanol, proposed other mechanisms for dioxene and dioxolane formation. They found that 1-(3-butyn-2-yloxy)-2-propanol (**1d**), the only propargyloxyethanol they examined that could not give a dioxene by the route shown in Scheme I, gave 2,3,5-trimethyl-1,4-dioxene (**7d**) as the major product; the only other product detected was 2-methylene-3,6-dimethyl-1,4-dioxane (**4d**). As **4d** and their other 2-methylene-1,4-dioxanes slowly isomerized to the

SCHEME I



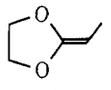
a, R = R_1 = R_2 = R_3 = H
b, R = CH_3; R_1 = R_2 = R_3 = H
c, R_1 = CH_3; R = R_2 = R_3 = H
d, R_1 = R_3 = CH_3; R = R_2 = H
e, R = R_1 = H; R_2R_3 = $(CH_2)_3$
f, R = R_1 = H; R_2R_3 = $(CH_2)_4$

(1) Taken from the Ph.D. Thesis of J. G. Maroski, University of California, Davis, 1971.

(2) A. T. Bottini, F. P. Corson, and E. F. Böttner, *J. Org. Chem.*, **30**, 2988 (1965).

(3) R. Faure and G. Descotes, *Bull. Soc. Chim. Fr.*, 1569 (1966).

corresponding 1,4-dioxenes under their reaction conditions, Faure and Descotes concluded that 1,4-dioxene formation took place by this route rather than cyclization of a 1-propynyloxyethanol (**3**). Significantly, it has been shown that thermal or hydroxide-induced isomerization of 2-methylene-1,4-dioxane (**4a**) could account for no more than a small fraction of the 2-methyl-1,4-dioxene (**7a**) obtained by treatment of propargyloxyethanol (**1a**) with sodium hydroxide in DMSO at 120°.[2] Negative evidence (they did not detect a 2-vinyl-1,3-dioxolane as a product from **1d** of **1f**) led the French workers to propose that 1,3-dioxolane formation occurred by cyclization of a 1-propynyloxyethanol to the corresponding ketene acetal (*e.g.*, **8**), followed by rearrangement of the double



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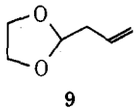
bond away from oxygen. It should also be noted here that Faure and Descotes did not detect a 3,6-dioxacycloheptene as a product from any of their reactions.

In order to determine the effect of alkyl substitution on the course of cyclization of propargyloxyethanols and, hopefully, clarify the mechanisms of 1,4-dioxene and 1,3-dioxolane formation, we examined base-induced cyclizations of the propargyloxyethanols **1a–1f**. Compounds **1d** and **1f** were also studied by Faure and Descotes. We treated **1b–1f** with KOH in water, DMSO, and *tert*-butyl alcohol (*t*-BuOH). In addition, **1c** was treated with KOH in triglyme, and **1c**, **1d**, and **1f** were treated with potassium *tert*-butoxide (KO-*t*-Bu) in *t*-BuOH. Under this range of conditions, **1c**, **1d**, and **1f** gave the four cyclic products corresponding to those obtained from **1a**. Compound **1b** also gave four cyclic ethers, which proved to be 2-allyl-1,3-dioxolane (**9**) and



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2-methyl-2-vinyl-1,3-dioxolane (**6c**) as well as the expected 1,3-dioxolane **6b** and 3,6-dioxacycloheptene **5b**. *trans*-2-Propargyloxycyclopentanol (**1e**) gave only the corresponding 3,6-dioxacycloheptane **5e** and 1,4-dioxene **7e**. The 3,6-dioxacycloheptenes, 1,3-dioxolanes, and 1,4-dioxenes were stable under the reaction and work-up conditions, but the 2-methylene-1,4-dioxanes were rearranged slowly to the corresponding dioxenes by base in DMSO, and **4f** rearranged rapidly to **7f** when heated above 120°.

Because of their possible involvement as intermediates in cyclizations of **1b** or **1c**, we also studied several reactions of the butadienyloxyethanols **2c**, **10**, and **11**.

$$\underset{\textbf{10}}{CH_2{=}C{=}CHCH_2OCH_2CH_2OH} \qquad \underset{\textbf{11}}{CH_2{=}\overset{\overset{CH_2}{\|}}{C}HCOCH_2CH_2OH}$$

The propargyloxy alcohols **1b–1f** were prepared by treatment of the appropriate propargyl alcohol with either base and ethylene bromohydrin or substituted epoxide or acid and substituted epoxide. Analysis by vpc of the acetate of 1-(3-butyn-2-yloxy)-2-propanol (**1d**) indicated that it was a 1:1 mixture of diastereomers. 2-(2,3-Butadien-1-yloxy)ethanol (**10**) was prepared from allenylcarbinyl chloride and ethylene glycol, and the isomeric butadienyloxyethanols **2c** and **11** were obtained as by-products from reactions in *t*-BuOH of 2-(3-butyn-2-yloxy)ethanol (**1c**) with KOH and KO-*t*-Bu, respectively.

The cyclic products were characterized by means of their ir and nmr spectra, and the new compounds, with the exception of **5f**, gave satisfactory elemental analyses. In addition, the 2-methylene-1,4-dioxanes (**4**) were isomerized to the corresponding 2-methyl-1,4-dioxenes (**7**) with KOH in DMSO, **7c** and **7f** were oxidized with mercuric acetate according to the method described by Summerbell, *et al.*,[4] for oxidation of 1,4-dioxene and **7a**, and the 2-vinyl- and 2-(1-propenyl)-1,3-dioxolanes were synthesized by literature procedures[5] for this class of compounds.

Cyclization of 1-(3-butyn-2-yloxy)-2-propanol (**1d**) in water gave a 2.1:1 mixture of the diastereomeric 2-methylene-3,5-dimethyl-1,4-dioxanes (**4d** and **4d′**) and a 1.6:1 mixture of the diastereomeric 4,7-dimethyl-3,6-dioxacycloheptenes (**5d** and **5d′**). As it seems reasonable that the trans isomers would be more stable and would form *via* lower energy transition states, the predominant diastereomers (**4d** and **5d**) are assigned the trans configuration. Significantly, **4d** and **5d** had the lower refractive indexes,[6] and the minor 2-methylene-3,5-dimethyl-1,4-dioxane (**4d′**) rearranged more rapidly than **4d** to 2,3,5-trimethyl-1,4-dioxene (**7d**) on treatment with KOH in DMSO. The diastereomeric 2,4-dimethyl-2-vinyl-1,3-dioxolanes (**6d** and **6d′**) were formed in a ratio of 1:1.5 from **1d** and 1.5:1 from acid-catalyzed condensation of ethylene glycol and methyl vinyl ketone. As the latter reaction conditions should give the equilibrium mixture (the major product had the lower refractive index[6]), and as the work of Rommelaere and Anteunis[7] indicates that the more stable diastereomer should have the *RR,SS* configuration (cis methyl groups), this configuration is assigned to the minor dioxolane from **1d**, *i.e.*, **6d**.

Reactions in Water.—The yields and compositions of cyclic products obtained from treatment of propargyloxyethanol (**1a**) and its alkyl-substituted homologs **1c–1f** with aqueous KOH are summarized in Table I. Note that the results obtained with **1a** are very similar to those obtained earlier[2] using NaOH.

Comparison of the results obtained with **1a** and **1c** shows that substitution of a methyl group at propargyl carbon results in a significant increase in the methylenedioxane (**4**):dioxacycloheptene (**5**) ratio and reduces the yield of dioxolane (**6**) to barely a trace. Further comparison with the results obtained with **1d** shows that substitution of a methyl at carbinol carbon leads to a further increase in the **4**:**5** product ratio.

The decrease in the amount of seven-membered ring product on substitution of a methyl group at propargyl carbon can be attributed to electronic and steric factors. The transition state **4c**‡ leading to 2-methylene-

(4) R. K. Summerbell, G. Kalb, E. Graham, and A. Allred, *J. Org. Chem.*, **27**, 4461 (1962).

(5) (a) H. Hibbert and M. S. Whelen, *J. Amer. Chem. Soc.*, **51**, 3115 (1929); (b) R. F. Fischer and C. W. Smith, *J. Org. Chem.* **25**, 319 (1960); (c) D. L. Heywood and B. Phillips, *ibid.*, **25**, 1699 (1960).

(6) H. Van Bekkum, A. Van Veen, R. Verkade, and B. Wepster, *Recl. Trav. Chim. Pays-Bas*, **80**, 1310 (1961).

(7) Y. Rommelaere and M. Anteunis, *Bull. Soc. Chim. Belg.*, **79**, 11 (1970).

TABLE I

YIELDS AND PRODUCT COMPOSITIONS FROM REACTIONS OF PROPARGYLOXYETHANOLS WITH AQUEOUS POTASSIUM HYDROXIDE[a]

Compd	Yield, %	Composition, % 4	5	6	7
1a[b]	54	36	44	20	2
1a	72	39	36	24	<1
1c	68	62	37	<1	<1
1d	72	87[c]	12[d]	<1	<1
1e	52	<1	95	<1	5
1f	98	93	3	4	<1

[a] Reaction mixtures were 2 *M* in 1 and 2 *M* in base, and reactions were carried out for 12 hr at reflux. [b] The base was NaOH. [c] As a 2.1:1 mixture of diastereomers. [d] As a 1.8:1 mixture of diastereomers.

3-methyl-1,4-dioxane is similar electronically to the transition state leading to **4a**. However, the transition state **5c**$^{\mp}$ leading to 7-methyl-3,6-dioxacycloheptene is destabilized relative to the transition state leading to **5a** because of the closer proximity of the methyl group at propargyl carbon to the developing negative charge on unsaturated carbon.

4c$^{\mp}$

5c$^{\mp}$

Because of the greater internal angle strain in seven-membered rings of first-row elements, substitution of a methyl group leads to a greater increase in energy due to nonbonded interactions than is the case when a methyl group is substituted for hydrogen at the less hindered position on a six-membered ring, *i.e.*, equatorial rather than axial. It is likely that part of this difference in nonbonded interactions is also responsible for the lower energy of **4c**$^{\mp}$ compared to **5c**$^{\mp}$. The view that steric factors are partly responsible for the decrease in importance of the seven-membered ring product that results on methyl substitution is consistent with the results obtained with the dimethyl-substituted propargyloxyethanol **1d**, which gives an even greater **4**:**5** product ratio.

The importance of steric factors in cyclizations of propargyloxyethanols was demonstrated dramatically by the markedly different courses of cyclization of *trans*-2-propargyloxycyclopentanol (**1e**) and *trans*-2-propargyloxycyclohexanol (**1f**). Nearly all of the product from the cyclopentane was the corresponding dioxacycloheptene **5e**, whereas the cyclohexane gave over a 90% yield of the corresponding 2-methylene-1,4-dioxane **4f**. It seems reasonable that the energy associated with the trans fusion of six- and five-membered rings, which would be reflected in the transition state leading to **4e**, is responsible for preferred cyclization of **1e** to **5e**. In contrast, the relatively strain-free trans-fused **4f** is formed in preference to **5f**.

No cyclic products were formed when either 2-(2-butyn-1-yloxy)ethanol (**1b**) or 2-(2,3-butadien-2-yloxy)ethanol (**2c**) were treated with refluxing aqueous KOH for 12 hr. More than 70% of the **1b** and **2c** was recovered unchanged. This shows that methyl substitution significantly slows nucleophilic addition at acetylenic or allenic carbon, and that **2c** is not rearranged to **1c** under these reaction conditions. Note that both **1b** and **2c** undergo cyclization when treated with base in nonaqueous solvents, and these reactions are discussed below.

Reactions in DMSO and in Triglyme.—In Table II are given the yields and compositions of cyclic products from treatment of the propargyloxyethanols **1a**–**1f** and related compounds with KOH in DMSO. Also included in Table II are similar data for reactions of **1a**, **1b**, and 2-(2,3-butadien-2-yloxy)ethanol (**2c**) with KOH in triglyme.

TABLE II

YIELDS AND PRODUCT COMPOSITIONS FROM REACTIONS OF PROPARGYLOXYETHANOLS AND RELATED COMPOUNDS WITH POTASSIUM HYDROXIDE IN DMSO OR TRIGLYME[a]

Compd/Solvent	Reaction time, hr	Yield, %	Composition, % 4	5	6	7
1a/DMSO[b]	0.7	33	4	7	18	71
1a/TG[c]	0.5	58	<1	2	12	86
1b/DMSO	0.5	48[d]		12	70	
10/DMSO	0.5	35[e]		19	67	
1c/DMSO	0.5	65	14	14	11	61
1c/TG[c]	0.7	72	10	6	7	76
2c/DMSO	4.1	80	3	2	45	50
2c/TG	9.2	84			32	68
11/DMSO	12	5			100	
1d/DMSO	0.1	80	32[f]	7[g]	23[h]	38
1e/DMSO	12	78		35		65
1f/DMSO	0.5	80			6	94

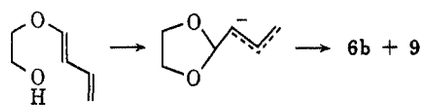
[a] Reaction mixtures were 2 *M* in compound and 2 *M* in KOH and reaction temperature was 100° unless noted otherwise. [b] Reference 2; base was NaOH. [c] Temperature 180–190°. [d] Includes 17% **9**. [e] Includes 14% **9**. [f] As a 2.4:1 mixture of diastereomers. [g] As a 1.3:1 mixture of diastereomers. [h] As a 1.5:1 mixture of diastereomers.

Before discussing the results in Table II, it should again be noted that the 2-methylene-1,4-dioxanes (**4**) undergo some rearrangement to the corresponding 2-methyl-1,4-dioxenes (**7**) in the presence of KOH in DMSO. For example, about half of the **4a** rearranges to **7a** in 0.7 hr when treated under the reaction conditions at 120°. In contrast and in confirmation of earlier results,[2] there is no significant rearrangement of **4a** to **7a** in 0.7 hr when the base is NaOH.[8]

The reactions of 2-(2-butyn-1-yloxy)ethanol (**1b**) and 2-(2,3-butadien-1-yloxy)ethanol (**10**) with KOH in DMSO gave similar mixtures of 2-methyl-3,6-dioxacycloheptene (**5b**), 2-(1-propenyl)-1,3-dioxolane (**6b**), and 2-allyl-1,3-dioxolane (**9**), and this indicates that these cyclizations occur by common pathways. As the per cent of the seven-membered ring product **5b** was significantly greater from the allene than from the acetylene, it seems likely that cyclization of the allene is the major pathway to **5b** from both **1b** and **10**, *i.e.*, **1b** → **10** → **5b**. This is consistent with results noted earlier which showed that methyl substitution on a carbon–carbon multiple bond slows nucleophilic addition. The isolation of nearly identical ratios of the dioxolanes **6b** and **9** from the acetylene **1b** and the allene **10** indicates that these products were formed from a

(8) This cation effect on base efficiency in DMSO has been observed by others. For example, D. J. Cram, C. A. Kingsbury, and B. Rickborn [*J. Amer. Chem. Soc.*, **83**, 3688 (1961)] reported that rates of racemization and isotope exchange decreased by about two powers of ten when NaO-*t*-Bu was used in place of KO-*t*-Bu in DMSO.

common intermediate, and the most likely intermediate is 2-(1,3-butadien-1-yloxy)ethanol (**12**) formed



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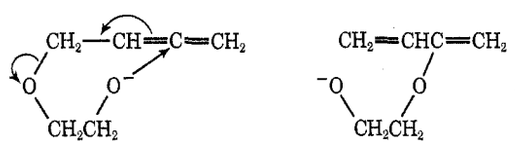
by prototropic rearrangement of **10**. In addition to the rearrangement of **1c** to 2-(1,3-butadien-2-yloxy)-ethanol (**11**) *via*, presumably, the allene isomer **2c** observed in this research, other examples of base-induced rearrangements of acetylenes or allenes to conjugated dienes are recorded in the literature.[9] Further, base-induced cyclizations analogous to that suggested for **12** have been observed for 1,3-cyclohexa-[10a] and 1,3-cycloheptadienyloxyethanol.[10b]

Interestingly, examination by vpc of the ether extracts of the reaction mixtures from **1b** and **10**, but not the distilled cyclic products, showed the presence of 2-methyl-2-vinyl-1,3-dioxolane (**6c**) in amounts which represented yields of 3–4% based on **1b** or **10**. The **6c** could not have arisen from 2-(2,3-butadien-2-yloxy)-ethanol (**2c**) because this compound yields **6c** and 2,3-dimethyl-1,4-dioxene (**7c**) in a 2.1:1 ratio in triglyme and a 1.1:1 ratio in DMSO under the reaction conditions, and no **7c** was obtained. It was found that 2-(1,3-butadien-2-yloxy)ethanol (**11**) cyclizes to only **6c** during vapor phase chromatography, and **11** is the likely source of the **6c** observed from the acetylene **1b** and allene **10**. A reasonable route to **11** is an S_N2' displacement of alkoxide by alkoxide on **10**.



Comparison of the results obtained with **1a** and **1c** in both DMSO and triglyme reveals that the most obvious result of substitution of a methyl group at propargyl carbon is a significant increase in the yields of the 2-methylene-1,4-dioxane and 3,6-dioxacycloheptene. This indicates that the inductive effect of the methyl group slows the rate of prototropic rearrangement of **1c** to 2-(2,3-butadien-2-yloxy)ethanol (**2c**) by destabilizing the intermediate carbanion. Thus, the importance of ring closure to **4c** and **5c** is enhanced.

Isolation of a significant amount of 2-methyl-2-vinyl-1,3-dioxolane (**6c**) from reactions of 2-(3-butyn-2-yloxy)ethanol (**1c**) in DMSO and in triglyme provides a decisive argument against the mechanism proposed by Faure and Descotes[3] for 2-vinyl-1,3-dioxolane formation because the required 2-(1-propynyloxy)ethanol (**3**) cannot be formed from **1c**.

Of even more significance was the large yield of 2,3-dimethyl-1,4-dioxene (**7c**) obtained from reactions of **1c** in DMSO and triglyme. Some of the **7c** formed in DMSO certainly arose by base-induced rearrangement of 2-methylene-3-methyl-1,4-dioxane (**4c**). However, only half of the **4c** rearranged to **7c** when a mixture of the four cyclic products from **1c** was treated with KOH under the reaction conditions for an extended period, *i.e.*, for 12 hr, rather than the 0.5-hr reaction time used for **1c**. Further, **4c** is stable in triglyme under the reaction conditions. Therefore, at least one intermediate other than the dioxane **4c** must be involved in the formation of **7c** from **1c**.

Insight into the mechanism of 2-methyl-1,4-dioxene (**7**) formation was gained by studying the behavior of 2-(2,3-butadien-2-yloxy)ethanol (**2c**) when treated with KOH in DMSO and triglyme. Reactions at 100° monitored by nmr spectroscopy revealed that 2-methyl-2-vinyl-1,3-dioxolane (**6c**) and 2,3-dimethyl-1,4-dioxene (**7c**) were formed as **2c** was destroyed. In addition to **6c** and **7c**, reaction of **2c** with KOH in DMSO gave small amounts of 2-methylene-3-methyl-1,4-dioxane (**4c**) and 7-methyl-3,6-dioxacycloheptene (**5c**) (3 and 2%, respectively), which indicates that slow isomerization of the allene **2c** to the acetylene **1c** occurs in this solvent. This shows as well that **4c** is not an important source of the dioxene **7c** from this reaction of **2c** because only a small amount of the stable seven-membered ring product **5c** was observed, and **4c** and **5c** are formed in a ratio of about 1:1 on cyclization of **1c**. The possibility that **2c** cyclizes directly to **4c** and/or **5c** seems unlikely because no evidence was obtained that indicated the presence of these cyclic products in the reaction mixture of **2c** in triglyme. It may be concluded therefore that **2c** cyclizes directly to **6c** and **7c** in triglyme, and that rearrangement of **2c** to **1c** does not occur to a significant extent in that solvent.

The results with **2c** clearly implicate this compound as the important intermediate in the formation of 2,3-dimethyl-1,4-dioxene (**7c**) from 2-(3-butyn-2-yloxy)-ethanol (**1c**) in triglyme. The different **7c**:**6c** ratios obtained from **1c** and **2c**, 11:1 and 2.1:1, can be explained on the basis of the more than 80° temperature difference at which the reactions were carried out. The small quantity of **2c** available required that the reaction be followed by means of nmr spectroscopy, and it was not practicable for us to attempt the reaction at 180–190°, the temperature range used for preparative scale runs with the propargyloxyethanols **1a** and **1c**. Comparison of the **7c**:**6c** product ratios obtained from **1c** and **2c** in DMSO, 5.5:1 and 1.1:1, indicates that the allene **2c** and, to a lesser extent, the methylenedioxane **4c** are both important as intermediates for **7c** from **1c** in that solvent.

It should be noted here that treatment of 2-(1,3-butadien-2-yloxy)ethanol (**11**) with KOH in DMSO at 100° did not give a detectable amount of either of the six-membered or seven-membered ring products. Presence of a small amount of 2-methyl-2-vinyl-1,3-dioxolane (**6c**) was indicated by vpc. However, it was shown subsequently that about 10% of the **11** cyclized to **6c** under the vapor phase chromatographic conditions. As the observed amount of **6c** was about 10% of the recovered **11**, it seems that the dioxolane **6c** was not formed in a significant amount by treatment with KOH in DMSO. Although **11** is not an intermediate in the base-induced cyclizations, its formation is important because it removes the allene intermediate **2c**

(9) For examples, see E. D. Bergmann, "The Chemistry of Acetylene and Related Compounds," Interscience, New York, N. Y., 1948, p 23; W. Smadja, *Ann. Chim. (Paris)*, **10**, 105 (1965), and references cited therein; H. A. Selling, J. A. Rompes, J. H. Van Boom, S. Hoff, L. Bradsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **88**, 119 (1969); J. A. Rompes, S. Hoff, P. P. Montijn, L. Bradsma, and J. F. Arens, *ibid.*, **88**, 1145 (1969).

(10) (a) A. T. Bottini, F. P. Corson, K. A. Frost, II, and W. Schear, *Tetrahedron*, **28**, 4701 (1972); (b) K. A. Frost, II, unpublished work.

from the reaction coordinate leading to **6c** and **7c**, thereby decreasing the yield of these products.

The importance of **2c** as an intermediate in formation of 2,3-dimethyl-1,4-dioxene (**7c**) indicates that allenyloxyethanol (**2a**) may be an important intermediate in formation of 2-methyl-1,4-dioxene (**7a**) as well as 2-vinyl-1,3-dioxolane (**6a**) from **1a** in nonaqueous solvents. Substitution of a methyl group for hydrogen at C_1 of allenyloxyethanol should favor formation of the dioxene by reducing its rate of formation less than the rate of formation of the dioxolane. This is consistent with the larger **7**:**6** product ratio seen for **1c**. On the other hand, if **2a** is the single important intermediate for formation of **7a**, the relative free energies of the transition states leading to **6a** and **7a** from **2a** are particularly sensitive to changes in solvent because the **6a**:**7a** product ratio changes from 20:1 in water to 1:4 in DMSO to 1:7 in triglyme.[2] This corresponds to a relative change in free energies of over 3.6 kcal. Although such a change is not out of reason, it seems difficult to rationalize. Therefore, in the absence of additional evidence, 2-(1-propynyloxy)ethanol (**3a**) should continue to be considered as a probable intermediate for formation of **7a** from propargyloxyethanol (**1a**). Significantly, the thioether analog of **3a**, 2-(1-propynylthio)ethanol, undergoes base-induced cyclization to 2,3-dihydro-5-methyl-1,4-oxathiin, and the thioether analog of allenyloxyethanol is not a significant intermediate in the reaction.[11]

Comparison of the behavior of the 1:1 mixture of diastereomeric 1-(3-butyn-2-yloxy)-2-propanols (**1d**) with that of **1c** on treatment with KOH in DMSO shows that substitution of carbinol carbon by a methyl group increases the yields of the dioxanes and dioxolanes and decreases the yields of the corresponding 3,6-dioxacycloheptenes and 1,4-dioxene. Increase in yield of the 1,4-dioxanes can be attributed to the greater nucleophilicity of the secondary alkoxide generated from **1d**, and the decrease in yield of the dioxacycloheptenes can be rationalized on the basis of increased steric hindrance in the seven-membered ring owing to the presence of the second methyl group. The increased yield of 1,3-dioxolanes and decreased yield of 1,4-dioxene can also be attributed to the increased nucleophilicity of the alkoxide. There should be less new carbon–oxygen bond formation in the transition states leading to **6d** and **7d** (**6d**$^{\mp}$ and **7d**$^{\mp}$) than in those leading to **6c** and **7c** (**6c**$^{\mp}$ and **7c**$^{\mp}$), and consequently there is likely to be less stabilizing allylic resonance developed in **7d**$^{\mp}$ than in **7c**$^{\mp}$. It should also be noted that part of the lower yield of the dioxene may be accounted for by the lesser tendency of the 2-methylene-1,4-dioxanes to rearrange.

On treatment with KOH in DMSO, the cyclopentane derivative **1e** gave a 35:65 mixture of the corresponding 3,6-dioxacycloheptene **5e** and dioxene **7e**, and the cyclohexane derivative **1f** gave a 6:94 mixture of the corresponding 2-vinyl-1,3-dioxolane **6f** and dioxene **7f**. Although the 3,6-dioxacycloheptene **5e** and the 1,3-dioxolane **6f** were undoubtedly formed by cyclization, respectively, of the starting propargyloxycyclopentanol **1e** and the allenyloxycyclohexanol **2f**, the origin of the two dioxenes is unclear. They could have been formed by cyclization of either or both of the corresponding allenyloxy alcohols (**2e** and **2f**) or 1-propynyloxy alcohols (**3e** and **3f**). In addition, part of the **7f** could have arisen by rearrangement of the dioxane **4f**, which is converted rapidly to **7f** under the reaction conditions. As the cyclopentane **1e** gave virtually none of the 1,4-dioxane **4e** on treatment with aqueous KOH, it is unlikely that **4e** is a significant intermediate in the formation of **7e**.

Reactions in *t*-BuOH.—Study of the effect of solvent on the course of base-induced cyclizations of the propargyloxyethanols was extended to include *t*-BuOH. Also, KO-*t*-Bu was used in addition to or in place of KOH with several of the proparglyoxyethanols. Based on the results of Price and Synder[12] and Cram and coworkers,[13] it was anticipated that the rates of prototropic rearrangement and the nucleophilicity of oxygen would be greater in *t*-BuOH than in water but less than in DMSO. Substitution of KO-*t*-Bu for KOH was expected to result in faster rates of prototropic rearrangement and, because of the greater effective alkoxide concentration, faster rates of nucleophilic addition. The results are summarized in Table III. Note that all of the cyclic products were stable under the reaction conditions.

TABLE III

YIELDS AND PRODUCT COMPOSITIONS FROM REACTIONS OF PROPARGYLOXYETHANOLS WITH BASE IN *t*-BuOH[a]

Compd	Base	Yield, %	Composition, % 4	5	6	7
1a	KOH	61	5	8	65	22
1b	KOH	15[b]		57	37	
1c	KOH	38	42	39	6	12
1c	KO-*t*-Bu	36	37	28	10	26
1d	KO-*t*-Bu	58	35[c]	7[d]	25[e]	33
1e	KOH	61		48		52
1f	KOH	80	31	4	13	52
1f	KO-*t*-Bu	82	12	2	21	65

[a] Reaction mixtures were 2 *M* in compound and 2 *M* in base, and reactions were carried out at reflux temperature for 12 hr. [b] Includes 5% **9**. [c] As a 1.8:1 mixture of diastereomers. [d] As a 1.9:1 mixture of diastereomers. [e] As a 1.4:1 mixture of diastereomers.

The compositions of the cyclic ethers obtained from **1a** and **1c**–**1f** with KOH in *t*-BuOH are clearly intermediate between those obtained in water and in DMSO. Substitution of KO-*t*-Bu for KOH gave compositions of cyclic ethers that were somewhat more similar to those formed in DMSO.

Interestingly, propargyloxyethanol (**1a**) gave 2-vinyl-1,3-dioxolane (**6a**) as the major product. This could be due to a slowing of the prototropic rearrangement of allenyloxyethanol (**2a**) to 1-propynyloxyethanol (**3a**) relative to its ring closure to **6a**. Alternatively, both **6a** and 2-methyl-1,4-dioxene (**7a**) could arise by cyclization of **2a**. The latter would require that the **6a**:**7a** product ratio from **3a** is a highly sensitive function of solvent, with the dioxolane **6a** being favored in hydroxylic solvents. The results seen with **1c** and **1d**, specifically the solvent dependence of the corresponding dioxolane:dioxene (**6**:**7**) ratio, require this latter explanation.

(11) A. T. Bottini and E. F. Böttner, *J. Org. Chem.*, **31**, 385 (1966).

(12) C. C. Price and W. H. Snyder, *ibid.*, **27**, 4639 (1962).

(13) D. J. Cram, B. Rickborn, and G. R. Knox, *J. Amer. Chem. Soc.*, **82**, 6412 (1960).

Significantly different ratios of dioxolane **6f** and dioxene **7f** were obtained from *trans*-2-propargyloxycyclohexanol (**1f**) with KOH and KO-*t*-Bu. This as well as the slightly different **4c**:**5c** ratios obtained from 2-(3-butyn-2-yloxy)ethanol (**1c**) on treatment with the two bases can be attributed to the fact that the reaction mixtures containing KOH also contain a small amount of water.

The results with 2-(2-butyn-1-yloxy)ethanol (**1b**) require only brief comment. 2-Methyl-3,6-dioxacycloheptene (**5b**) accounts for a much higher per cent of the products in *t*-BuOH than in DMSO, and the 2-(1-propenyl)-2-allyl-1,3-dioxolane (**6b**:**9**) product ratio is raised from 4.1:1 to *ca* 7:1.

During the course of the work with 2-(3-butyn-2-yloxy)ethanol (**1c**), it was observed that the per cent of 2-methyl-2-vinyl-1,3-dioxolane (**6c**) present in the distilled product fraction was substantially less than that indicated by vpc analysis of the ether extract of the reaction mixture. Careful fractionation of the reaction mixture led to isolation of 2-(2,3-butadien-2-yloxy)ethanol (**2c**) and fractions enriched in 2-(1,3-butadien-2-yloxy)ethanol (**11**). When subjected to the conditions used for chromatographic analysis, both **2c** and **11** gave **6c**. Similar observations were noted with the diastereomeric 1-(3-butyn-2-yloxy)-2-propanols (**1d**). Subsequent examination of the reaction mixtures indicated the presence of 1-(1,3-butadien-2-yloxy)-2-propanol, which cyclized on gas chromatography to a 1:1 mixture of the diastereomeric 2,4-dimethyl-2-vinyl-1,3-dioxolanes (**6d** and **6d'**).

Experimental Section

Temperatures are uncorrected. Ir spectra were obtained with a Beckman IR-8 spectrophotometer; spectra of samples available in only microliter quantities were obtained using micro-NaCl plates and a beam condenser. Unless stated otherwise, nmr spectra were obtained of CCl_4 solutions with a Varian Associates A-60A spectrometer; resonance frequencies in nmr spectra were determined relative to 1–2% internal tetramethylsilane. Vpc chromatograms were obtained with an Aerograph Model A-700 or A-90. Mass spectra were determined with a Consolidated Electrodynamics Corp. Type 21-104 mass spectrometer; an ionizing voltage of 70 eV was used. Microanalyses were performed at the Microanalytical Laboratory, University of California, Berkeley, and Galbraith Laboratories, Inc., Knoxville, Tenn. Potassium *tert*-butoxide (KO-*t*-Bu) was obtained from MSA Research Corp. The KOH used was Mallinckrodt 85% minimum assay.

2-(2-Butyn-1-yloxy)ethanol (1b).—To a rapidly stirred suspension prepared from 47 g (<0.71 mol) of coarsely powdered KOH and 100 g (1.43 mol) of 2-butyn-1-ol maintained at 10° under a Dry Ice reflux condenser was added dropwise 79 g (0.71 mol) of ethylene bromohydrin. During the addition KBr precipitated. When the addition was complete the cooling bath was removed, and the temperature of the mixture rose to 40° in 45 min. When the reaction was no longer exothermic, the mixture was heated at 70–80° for 1 hr. The KBr was removed by filtration and washed with ether (100 ml). The filtrate containing the ether wash consisted of two layers. The heavy layer, which was miscible with water, and the ether solution were distilled to give a forerun of 2-butyn-1-ol and 48.6 g (60%) of 2-(2-butyn-1-yloxy)ethanol (**1b**): bp 75° (4 mm); n^{24}D 1.4586; nmr δ 4.08 (q, J = 2.3 Hz, 2, $CH_2C{\equiv}C$), 3.57 (m, 4, OCH_2CH_2O), 3.32 (s, 1, OH), and 1.83 ppm (t, J = 2.3 Hz, 3, $C{\equiv}CCH_3$).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.05; H, 8.71.

2-(3-Butyn-2-yloxy)ethanol (1c) was prepared as described for **1b** from 104 g (>1.58 mol) of KOH, 217 g (3.10 mol) of 3-butyn-2-ol, and 191 g (1.53 mol) of ethylene bromohydrin. The yield was 111 g (63%) of **1c**: bp 72–73° (12 mm); n^{22}D 1.4418; nmr δ 4.17 (q, d, J = 7 and 2 Hz, 1, CHO), 3.17–3.95 (m, 4, CH_2CH_2), 3.13 (s, 1, OH), 2.42 (d, J = 2 Hz, 1, $HC{\equiv}C$), 1.41 ppm (d, J = 7 Hz, 3, CH_3).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 62.88; H, 8.85.

1-(3-Butyn-2-yloxy)-2-propanol (1d) was prepared in 33% yield as described by Faure and Descotes:[3] bp 72–74° (14 mm); n^{23}D 1.4362 (lit.[3] bp 168°; n^{25}D 1.4365); nmr δ 2.88–4.27 (m, 4, $CHOCH_2CH$), 2.48 (s, 1, OH), 2.33 (d, J = 2 Hz, 1, $HC{\equiv}$), 1.38 (d, J = 6 Hz, 3, CH_3), 1.08 ppm (d, J = 6 Hz, 3, CH_3).

The acetate was prepared in 93% yield from 10 g of **1d** using the procedure of Marmor:[14] bp 55–58° (3 mm); $n^{22.6}$D 1.4269; nmr δ 4.58–5.13 (m, 1, $OCHCH_2O$), 3.85–4.27 (m, 1, $OCHC{\equiv}$), 3.14–3.73 (m, 2, OCH_2), 2.32 (d, J = 2.5 Hz, 1, $C{\equiv}CH$), 1.93 (s, 3, CH_3CO), 1.36 (d, J = 6.6 Hz, 3, CH_3), 1.18 ppm (d, J = 6.6 Hz, 3, CH_3).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.50; H, 8.31. Found: C, 63.35; H, 8.22.

Analysis by vpc using a 24-ft TCEP column at 82° indicated the presence of the two diastereomeric acetates in a ratio of 49:51, assuming equal detector sensitivity for the two stereoisomers.

***trans*-2-Propargyloxycyclopentanol (1e).**—Using a procedure patterned after that described[3] for preparation of **1f**, 150 g of cyclopentene oxide was converted in 54% yield to **1e**: bp 78–79° (1.5 mm); n^{22}D 1.4803; nmr δ 4.07 (d, J, = 2 Hz, 2, $CH_2C{\equiv}C$), 3.62–4.15 (m, 2, OCHCHO), 3.37 (s, 1, OH), 2.36 (t, J = 2 Hz, 1, $HC{\equiv}C$), 1.27–2.12 ppm [m, 6, $(CH_2)_3$].

Anal. Calcd for $C_8H_{12}O_2$: C, 68.59; H, 8.57. Found: C, 68.47; H, 8.68.

***trans*-2-Propargyloxycyclohexanol (1f)** was prepared in 79% yield from 115 g of cyclohexene oxide by the method of Faure and Descotes:[3] bp 86–87° (3 mm); n^{22}D 1.4821 [lit.[3] bp 120° (20 mm); n^{22}D 1.4790]; nmr δ 4.23 (d, J = 2.5 Hz, 2, $CH_2C{\equiv}C$), 3.32 (m, 2, OCHCHO), 3.08 (s, 1, OH), 2.40 (t, J = 2.5 Hz, 1, $HC{\equiv}C$) 0.83–2.33 ppm [m, 8, $(CH_2)_4$].

2-(2,3-Butadien-1-yloxy)ethanol (10).—To a rapidly stirred mixture of 35.5 g (0.40 mol) of allenylcarbinyl chloride[15] and 22 g of dry ethylene glycol under nitrogen at 30–40° was added dropwise a solution prepared from 9.2 g (0.40 mol) of sodium and 248 g of dry ethylene glycol. When the addition was complete the stirred mixture was heated at 75° for 6 hr, cooled, and stirred at room temperature for 9 hr. The mixture was added to 250 ml of water and extracted with ether (4 × 100 ml). The organic phases were combined, dried (K_2CO_3), and distilled to give 6.4 g (95% pure, 13%) of **10**, bp 92–106° (25 mm). An analytical sample was obtained by preparative vpc on XF-1150: n^{24}D 1.4688; nmr δ 4.98–5.43 (m, 1, $CH_2CH{=}$), 4.62–4.82 (m, 2, $={C=}CH_2$), 4.00 (d, t, J = 2.5 and 6.6 Hz, 2, $OCH_2CH{=}C$), and 3.37–3.74 ppm (m, 5, CH_2CH_2OH).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.18; H, 8.77. Found: C, 62.95; H, 8.96.

Reactions of the Proparagyloxyethanols (1a–1f) and 10 with Base.—*tert*-Butyl alcohol (*t*-BuOH) was distilled immediately before use, bp 82–83°. Freshly distilled dimethyl sulfoxide (DMSO), bp 84° (20 mm), was passed over Woelm neutral alumina, activity grade I, into a dry reaction vessel immediately before use; 15 g of alumina was used for each 40 ml of DMSO.

For all reactions carried out in water, *t*-BuOH, or DMSO, the reaction mixture was 2 *M* in **1** or **10** and 2 *M* in base. Reactions in water or *t*-BuOH were carried out at reflux temperature, those in DMSO at 100 ± 5°. The cooled *t*-BuOH and DMSO reaction mixtures were added to 1–3 volumes of water, and all aqueous solutions were extracted continuously with ether for 8–12 hr. The reaction of **1c** with KOH in triglyme was carried out as described for propargyloxyethanol (**1a**).[2] Ether solutions were dried (NaOH), analyzed by vpc, and distilled. The distilled product mixtures were again analyzed by vpc, and these analyses were checked by nmr and, in some cases, ir spectroscopy.

2-(2,3-Butadien-2-yloxy)ethanol (2c).—A mixture of 10.0 g (0.152 mol) of KOH, 75.0 ml of *t*-BuOH, and 17.5 g (0.153 mol) of **1c** was heated under reflux for 9.5 hr. In addition to the cyclic products, work-up gave a 0.3-g fraction with bp 73–78° (13 mm): ir 1945 cm^{-1} (s, C=C=C); nmr δ 5.24 (q, J = 3 Hz, $C{=}C{=}CH_2$), 3.60 (s, broad, CH_2CH_2), 2.92 (s, OH), and 1.87

(14) S. Marmor, "Laboratory Guide for Organic Chemistry," D. C. Heath, Boston, Mass., 1964, p 272.

(15) Prepared by Dr. J. E. Christensen according to the procedure of W. H. Carothers, G. J. Bercket, and A. M. Collins, *J. Amer. Chem. Soc.*, **54**, 4066 (1932).

ppm (t, J = 3 Hz, CH_3). Bands due to 2-(1,3-butadien-2-yloxy)ethanol (11) were also present in the ir and nmr spectra. Analysis by nmr, which was in accord with vpc analysis on XF-1150, indicated that the fraction was a 2:1 mixture of **2c** and **11**.

2-(1,3-Butadien-2-yloxy)ethanol (11).—A mixture of 17.1 g (0.155 mol) of KO-*t*-Bu, 75.0 ml of *t*-BuOH, and 17.2 g (0.151 mol) of **1c** was heated under reflux for 8 hr. In addition to the cyclic products, work-up gave 1.4 g (8%) of **11**: bp 66° (6 mm); mass spectrum *m/e* (rel intensity) 99 (20), 87 (38), 71 (74), 55 (60), 53 (45), 45 (29), 43 (100), 42 (28), 39 (24), 29 (24), 15 (30); uv λ_{max} 2320 Å (ϵ 10,000); nmr (20% in PhH) δ 5.54–6.42 (m, 2, $CH{=}CH_2$), 4.96–5.13 (m, 1, $=CHC{=}$), 4.08 (s, 2, $C{=}CH_2$), 3.62 (broad s, 4, CH_2CH_2), and 3.17 ppm (s, 1, OH).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 62.69; H, 8.88.

Reactions of 2-(2,3-Butadien-2-yloxy)ethanol (2c). A. With KOH in DMSO.—A heavy-walled nmr tube was charged under nitrogen with 92 μl of DMSO, 11.7 mg (0.177 mmol) of KOH, 7.7 mg of PhH (internal standard), and 19.9 mg of a 2:1 mixture of **2c** and **11**. The tube was sealed and, after the nmr spectrum of the mixture was taken, placed in an ethylene glycol bath maintained at 100° by the vapors of boiling water. From time to time the tube was removed from the bath and cooled, and the extent of the reaction was determined by nmr. The decrease in area of the triplet due to the methyl of **2c** and the increase in the areas of the singlets due to the methyls of 2-methyl-2-vinyl-1,3-dioxolane (**6c**) and 2,3-dihydro-5,6-dimethyl-1,4-dioxene (**7c**) were monitored for 6 hr, at which time all of the **2c** had reacted to give an 80% yield of a mixture that consisted of 3% **4c**, 2% **5c**, 45% **6c**, and 50% **7c**.

B. With KOH in Triglyme.—Following the procedure for the reaction in DMSO, a mixture of 96 μl of triglyme, 21.1 mg of a 2:1 mixture of **2c** and **11**, and 12.1 mg (0.184 mmol) of KOH was heated at 100°, and the extent of the reaction was determined from time to time by nmr. After 16.7 hr, the reaction mixture was analyzed by vpc using 1,4-dioxane as internal standard; 83% of the **2c** had reacted, and the combined yield of **6c** and **7c** in a 1:1.1 ratio was 84%.

Reactions of 2-(1,3-Butadien-2-yloxy)ethanol (11). A. With KOH in DMSO.—A stirred mixture of 504 mg (4.4 mmol) of **11**, 284 mg (4.30 mmol) of KOH, and 2.2 ml of DMSO was heated at 100° for 12 hr. The reaction mixture was cooled and added to 25 ml of water, and the aqueous mixture was extracted with PhH (5 × 8 ml). Vpc analysis and use of a calibration curve prepared from solutions of **9c** in PhH indicated that up to 26 mg (5%) of **6c** could have been present in the PhH extract. In order to estimate the amount of unreacted **11**, a calibration curve was prepared using solutions of 2-(3-butyn-2-yloxy)ethanol (**1c**) in PhH. It was estimated that 243 mg (48%, uncorrected for sensitivity differences) of **11** was unchanged. That the material was **11** was confirmed by determination of its mass spectrum. Also present in the phH extract was a significant amount of high-boiling material, which was not identified.

B. With KO-*t*-Bu in *t*-BuOH.—A mixture of 496 mg (4.4 mmol) of **12**, 506 mg (4.5 mmol) of KO-*t*-Bu, and 2.2 ml of *t*-BuOH was heated under reflux for 12 hr. Analysis of the PhH extract of the reaction mixture by vpc using the previously constructed calibration curves indicated that up to 30 mg (6%) of **6c** could have been present in the extract in addition to 292 mg (59%, uncorrected for sensitivity differences) of **11**. The identity of **11** was confirmed by determination of its mass spectrum.

Characterization of Cyclization Products.—Summarized below are pertinent data for individual compounds. The stationary phase of the vpc column used for purifying the compound is given in parentheses. Unless a compound was isolated in a relatively pure state (>97%) by distillation, its boiling point is not given.

2-Methylene-3-methyl-1,4-dioxane (4c) (XF-1150) had $n^{22}D$ 1.4476; ir 1650 cm^{-1} (m); nmr δ 4.35 (m, 1, C=CH), 4.16 (m, 1, C=CH), 3.50–4.14 (m, 5, OCH_2CH_2OCH), and 1.28 ppm (d, J = 6.5 Hz, 3, CH_3).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.12; H, 9.02.

***trans*-3-Methylene-2,5-dimethyl-1,4-dioxane (4d)** (XF-1150 and TCEP) had $n^{23}D$ 1.4415; ir 1645 cm^{-1} (s); nmr (TMS) δ 4.36 (narrow m, 1, C=CH), 4.14 (narrow m, 1, C=CH), 3.10–4.04 (m, 4, $OCHCH_2OCH$), 1.25 (d, J = 6 Hz, 3, $OCHCH_3C{=}$), and 1.07 ppm (d, J = 6 Hz, 3, $OCHCH_3CH_2O$).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.65; H, 9.37. Found: C, 65.71; H, 9.62.

***cis*-3-Methylene-2,5-dimethyl-1,4-dioxane (4d′)** (XF-1150) had $n^{23}D$ 1.4426; ir 1645 cm^{-1} (s); nmr (TMS) δ 4.28 (s, 1, C=CH), 4.06 (s, 1, C=CH), 3.12–4.22 (m, 4, $OCHCH_2OCH$), 1.26 (d, J = 6.5 Hz, 3, $OCHCH_3C{=}$), and 1.16 ppm (d, J = 6.5 Hz, 3, $OCHCH_3CH_2O$).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.65; H, 9.37. Found: C, 65.48; H, 9.52.

2,5-Dioxa-3-methylene-*trans*-bicyclo[4.4.0]decane (4f) had bp 68° (2 mm); ir 1645 cm^{-1} (s); nmr δ 4.33 (s, 1, C=CH), 4.10 (s, 3, OCH_2 and C=CH), 2.67–3.77 (m, 2, OCHCHO), and 0.5–2.34 ppm [m, 8, $(CH_2)_4$].

Anal. Calcd for $C_9H_{14}O_2$: C, 70.07; H, 9.16. Found: C, 70.10; H, 9.15.

The methylene-1,4-dioxanes **4c**, **4d**, **4d′**, and **4f** were also converted to the corresponding methyl-1,4-dioxenes by treatment with KOH in DMSO (see Stability Studies below).

2-Methyl-3,6-dioxacycloheptene (5b) (XF-1150) had $n^{25}D$ 1.4636; ir 1677 cm^{-1} (vs); nmr δ 4.62 (t, q, J = 5 and 1 Hz, 1, $CH_2CH{=}CCH_3$), 3.59–4.02 (m, 6, $OCH_2CH_2OCH_2$), 1.72 ppm (d, J = 1 Hz, 3, CH_3).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 62.94; H, 8.87.

7-Methyl-3,6-dioxacycloheptene (5c) (XF-1150) had $n^{22}D$ 1.4489; ir 1650 cm^{-1} (vs); nmr δ 6.12 (d, d, J = 8 and 2 Hz, 1, OCH=C), 4.45 (d, d, J = 8 and 2 Hz, 1, OCH=CH), 3.25–4.33 (m, 5, $CHOCH_2CH_2O$), and 1.22 ppm (d, J = 8 Hz, 3, CH_3).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.24; H, 8.94.

***trans*-4,7-Dimethyl-3,6-dioxacycloheptene (5d)** (XF-1150) had $n^{22.5}D$ 1.4469; ir 1640 cm^{-1} (s); nmr (TMS) δ 5.93 (d, m, J = 6 Hz, 1, OCH=C), 4.08–4.58 (m, 3, CH_2CHCH_3O, CH=CH-$CHCH_3$), 3.64–3.72 (m, 2, OCH_2CH), and 1.15 ppm (d, J = 6.0 Hz, 6, $OCHCH_3C{=}$, $OCHCH_3CH_2$).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.65; H, 9.37. Found: C, 65.49; H, 9.61.

***cis*-4,7-Dimethyl-3,6-dioxacycloheptene (5d′)** (XF-1150) had ir 1645 cm^{-1} (s); nmr (TMS) δ 6.15 (d, d, J = 7.5 and 2.4 Hz, 1, OCH=C), 3.05–4.37 (m, 4, $OCHCH_2OCH$), 1.20 (d, J = 6.5 Hz, 3, $OCHCH_3C{=}$), and 1.13 ppm (d, J = 6.5 Hz, 3, $OCHCH_3CH_2O$).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.65; H, 9.37. Found: C, 65.74; H, 9.39.

2,6-Dioxa-*trans*-bicyclo[5.3.0]dec-3-ene (5e) (XF-1150) had $n^{23}D$ 1.4842; ir 1655 cm^{-1} (s); nmr δ 6.15 (d, m, J = 7.5 Hz, 1, OCH=C), 4.33–4.57 (m, 1, $OCH{=}CHCH_2$), 3.35–4.09 (m, 4, OCH_2, OCHCHO), and 1.36–2.27 ppm [m, 6, $(CH_2)_3$].

Anal. Calcd for $C_8H_{12}O_2$: C, 68.59; H, 8.57. Found: C, 68.37; H, 8.64.

2,6-Dioxa-*trans*-bicyclo[5.4.0]undec-3-ene (5f) (Carbowax, isolated as a 1:1 mixture with **7f**) had nmr δ 6.32 (d, t, J = 7 and ~0.5 Hz, 1, OCH=C), 4.84 (d, t, J = 7 and ~0.5 Hz, 1, OCH=CH), 3.92–4.30 (m, 2, $OCH_2C{=}$), 2.83–3.84 (m, OCHCHO, both isomers), 0.87–2.50 [m, $(CH_2)_4$, both isomers].

2-(1-Propenyl)-1,3-dioxolane (6b) was identical with the product obtained by the method of Heywood and Phillips:[5c] bp 141°; $n^{24}D$ 1.4407 (lit.[16] bp 147°; lit.[5c] $n^{30}D$ 1.4380); nmr δ 4.98–5.93 (m, 3, $CHCH{=}CHCH_3$), 3.56–4.04 (m, 4, OCH_2CH_2O), and 1.73 ppm (d, d, J = 5.8 and 0.6 Hz, 3, CH_3).

2-Methyl-2-vinyl-1,3-dioxolane (6c) was identical with the product obtained in 36% yield from methyl vinyl ketone and ethylene glycol using the method of Fischer and Smith:[5b] bp 110–112° [lit.[17] bp 111–112° (70 mm)]; $n^{23}D$ 1.4201; nmr δ 4.90–5.96 (m, 3, $CH{=}CH_2$), 3.68–3.92 (m, 4, OCH_2CH_2O), and 1.35 ppm (s, 3, CH_3).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.14; H, 8.75.

The diastereomeric **2,4-dimethyl-2-vinyl-1,3-dioxolanes (6d** and **6d′)** (XF-1150) were identical with the products with bp 77–78° (128 mm) obtained in a combined yield of 32% from methyl vinyl ketone and propylene glycol by the method of Fischer and Smith.[5b] The *RR,SS* isomer (more stable form, **6d**) had $n^{23}D$ 1.4133; nmr δ 4.92–6.08 (m, 3, $CH{=}CH_2$), 3.77–4.35 (m, 2, OCH_2CHO), 3.18–3.54 (m, 1, OCH_2CHO), 1.36 (s, 3, $CCH_3CH{=}$), and 1.20 ppm (d, J = 6 Hz, CH_2CHCH_3).

(16) J. P. Fourneau and S. Chantalou, *Bull. Soc. Chim. Fr.*, **12**, 845 (1945).

(17) J. Martinez Madrid and J. L. Mateo, *Markromol. Chem.*, **136**, 113 (1970).

TABLE IV

RESULTS OF STABILITY STUDIES OF CYCLIC PRODUCTS SUBJECTED TO BASE-INDUCED CYCLIZATION CONDITIONS[a]

Substituents	Solvent	Recovery, %	Initial composition %				Final composition %			
			4	5	6	7	4	5	6	7
a[b-d]	DMSO		38	36	22	4	21	34	20	25
a[b,d,e]	DMSO		38	36	22	4	3	33	23	41
a[b-d,f]	DMSO		38	36	22	4	40	36	20	4
a[b,d,f,g]	DMSO		38	36	22	4	29	36	20	16
c[c,h]	TG[i]	80	61	36	<1	3	63	32	<1	4
c[c,h]	DMSO	71	61	36	<1	3	31	31	<1	38
d	H_2O	70	65	9	26	<1	65	10	24	<1
d[j]	*t*-BuOH	68	24	11	44	20	27	12	37	24
d	DMSO	76	65	9	26	<1	2	4	25	69
e	H_2O	75	0	38	0	62	0	41	0	59
e	*t*-BuOH	94	0	38	0	62	0	38	0	62
e	DMSO	96	0	38	0	62	0	38	0	62
e[j]	DMSO	89	0	38	0	62	0	28	0	71
f	*t*-BuOH	78	>99	0	0	0	>99	0	0	0
f	DMSO	74	>99	0	0	0	<2	0	0	98

[a] Unless noted otherwise base was KOH, temperature was 100° in DMSO, 190° in triglyme, and reflux temperature in water and *t*-BuOH, reaction time was 12 hr, and a 1:1 mole ratio of base:cyclic product mixture was used. [b] Temperature 120°. [c] Reaction time 0.7 hr. [d] A 1:2 mole ratio of base:**4a** was used. [e] Reaction time 4.8 hr. [f] Base was NaOH. [g] Reaction time 4.4 hr. [h] Temperature 190°; sealed tube. [i] 90 mol % triglyme–10 mol % *t*-BuOH. [j] Base was KO-*t*-Bu.

Anal. Calcd for $C_7H_{12}O_2$: C, 65.64; H, 9.37. Found: C, 65.58; H, 9.94.

The *RS,SR* isomer (less stable form, **6d′**) had $n^{23}D$ 1.4154; nmr δ 4.91–6.11 (m, 3, $CH{=}CH_2$), 3.86–4.42 (m, 2, OCH_2CHO), 3.14–3.46 (m, 1, OCH_2CHO), 1.32 (s, 3, $CCH_3CH{=}$), and 1.18 ppm (d, J = 6 Hz, 3, CH_2CHCH_3).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.64; H, 9.37. Found: C, 65.83; H, 9.62.

7,9-Dioxa-8-vinyl-*trans*-bicyclo[4.3.0]nonane (6f).—Treatment of 2.0 g (0.105 mol) of 7,9-dioxa-8-(2-chloroethyl)-*trans*-bicyclo-[4.3.0]nonane, which was prepared in 52% yield from *trans*-1,2-cyclohexanediol, acrolein, and gaseous hydrogen chloride according to the method of Hibbert and Whelan,[5a] with 11.9 g of KO-*t*-Bu in 100 ml of DMSO at 77° for 3 hr gave a 14% yield of **6f**, which was identical with the product obtained from **1f**: bp 70–72° (6 mm); $n^{23}D$ 1.4671; nmr δ 4.80–6.20 (m, 4, $CHCH{=}CH_2$), 2.57–3.50 (m, 2, OCHCHO), and 0.42–2.50 [m, 8, $(CH_2)_4$].

Anal. Calcd for $C_9H_{14}O_2$: C, 70.09; H. 9.15. Found: C, 69.88; H, 9.19.

2-Allyl-1,3-dioxolane (9)[18] (XF-1150) had $n^{25}D$ 1.4366; nmr δ 5.45–6.12 (m, 1, $CH{=}CH_2$), 4.85–5.23 (m, 2, $CH{=}CH_2$), 4.77 (t, J = 4.8 Hz, $CHCH_2$), 3.69–3.94 (m, 4, OCH_2CH_2O), and 2.22–2.46 ppm (m, 2, $CH_2CH{=}$).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.03; H, 8.85.

2,3-Dimethyl-1,4-dioxene (7c) (XF-1150) had $n^{22}D$ 1.4474; ir 1700 cm^{-1} (s); nmr δ 3.92 (s, 4, OCH_2CH_2O) and 1.67 ppm (s, 6, $CH_3C{=}CCH_3$).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.37; H, 9.12.

Treatment of 2.31 g (0.0203 mol) of **7c** with 6.30 g (0.0197 mol) of mercuric acetate according to the method of Summerbell, *et al.*,[4] gave 3.42 g (87%) of mercury and 1.61 g (95%) of butane-2,3-dione. Ethylene glycol was also detected (vpc on Poropak Q) as a product, but its yield was not determined.

2,3,5-Trimethyl-1,4-dioxene (7d) (XF-1150) had $n^{23}D$ 1.4416 (lit.[3] bp 140°; $n^{25}D$ 1.4335); ir and nmr in excellent agreement with data reported by Faure and Descotes.[3]

2,5-Dioxa-3-methyl-*trans*-bicyclo[4.3.0]non-3-ene (7e) (XF-1150) had $n^{22}D$ 1.4710; ir 1673 cm^{-1} (s); nmr δ 5.62 (q, J = 1.3 Hz, 1, C=CH), 3.32–3.85 (m, 2, OCHCHO), 1.20–2.20 ppm [m with superimposed d at 1.63 ppm, J = 1.3 Hz, 9, $(CH_2)_3$ and CH_3].

(18) Synthesis of **9** has been claimed by U. Faass and H. Hilgert, *Chem. Ber.*, **87**, 1343 (1954).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.59; H, 8.57. Found: C, 68.81; H, 8.63.

2,5-Dioxa-3-methyl-*trans*-bicyclo[4.4.0]dec-3-ene (7f) had bp 50–51° (2.5 mm); $n^{23}D$ 1.4750 [lit.[3] bp 92° (18 mm); $n^{25}D$ 1.4772]; ir and nmr in excellent agreement with data reported by Faure and Descotes.[3] Treatment of 3.23 g (0.021 mol) of **7f** with 6.32 g (0.0198 mol) of mercuric acetate according to the method of Summerbell, *et al.*,[4] gave 3.75 g (94%) of mercury and 2.23 g (97%) of *trans*-1,2-cyclohexanediol, which was free of its cis isomer as determined by vpc on 4% Sorbitol–16% silicone 703.

Stability Studies.—Examination of the stability of the cyclic products was conducted under conditions that closely approximated the reaction conditions used for their preparation; generally, a mixture of the cyclic products was heated with base in water at reflux, in *t*-BuOH at reflux, in triglyme at 190°, or in DMSO at 100 or 120°. The work-up procedure was identical with that described for the cyclization reactions. Results are summarized in Table IV.

Registry No.—**1b,** 38644-91-6; **1c,** 18668-75-2; **1d,** 3973-21-5; **1d** acetate, 38653-27-9; **1e,** 38653-28-0; **1f,** 7229-32-5; **2c,** 38653-30-4; **4c,** 28125-74-8; **4d,** 38653-32-6; **4d′,** 38653-33-7; **4f,** 38653-34-8; **5b,** 38653-35-9; **5c,** 38653-36-0; **5d,** 38653-37-1; **5d′,** 38653-38-2; **5e,** 38653-39-3; **5f,** 38653-40-6; **6b,** 4528-26-1; **6c,** 26924-35-6; **6d,** 38653-43-9; **6d′,** 38653-44-0; **6f,** 38653-45-1; **7c,** 25465-18-3; **7e,** 38653-47-3; **7f,** 7196-96-5; **9,** 38653-49-5; **10,** 38653-50-8; **11,** 38653-51-9; 2-butyn-1-ol, 764-01-2; ethylene bromohydrin, 540-51-2; 3-butyn-2-ol, 2028-63-9; cyclopentene oxide, 285-67-6; allenylcarbinyl chloride, 25790-55-0; ethylene glycol, 107-21-1; methyl vinyl ketone, 78-94-4.

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