1,1-Di-*p*-tolyl-2-methyl-1,2-propanediol (II) was synthesized by the addition of 0.20 mole of ethyl α-hydroxyisobutyrate to 0.58 mole of *p*-tolylmagnesium bromide in 900 ml of anhydrous ether. The ester was pretreated by shaking with 3 g of sodium hydride in 20 ml of ether and was then filtered directly into the dropping funnel. Following the dropwise addition of the ester solution to the mechanically stirred Grignard solution, the reaction mixture was refluxed for 2 hr and then stirred at room temperature overnight. After hydrolysis, ethereal extraction, and drying of the organic layer over magnesium sulfate, the concentrated oil was vacuum distilled. The material boiling at 184–187° (3.5 mm) (38.5 g of 72% yield) was taken as product. The product crystallized to colorless prisms, mp 78.5–80°.

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.18; H, 7.98.

3,3-Di-*p*-tolyl-2-butanone (III).—Since product identification in the di-*p*-tolyl-dimethyl ethylene glycol system was carried out by peak enhancement gas phase chromatography, it was necessary to have available authentic samples of the possible pinacolones. The pinacolone rearrangement of 12.4 g of 2,3-di-*p*-tolyl-2,3-butanediol in 2.0 g of *p*-toluenesulfonic acid and 45 ml of glacial acetic acid was carried out by heating at reflux for 2.5 hr. After neutralization of the reaction mixture with aqueous sodium carbonate, ether extraction, and drying with sodium sulfate, the concentrated product layer was distilled under vacuum. Authentic III distilled at 197–200° (14 mm) (84% yield) and vpc analysis indicated that it was homogeneous. A single nonconjugated carbonyl at 1700 cm^{-1} was observed in the infrared spectrum. A semicarbazone was prepared, mp 178°, from ethanol–water.

Anal. Calcd for $C_{19}H_{23}N_3O$: N, 13.57; Found: N, 13.41.

A 2,4-dinitrophenylhydrazone, recrystallized from methanol, melted at 145–146°.

Anal. Calcd for $C_{24}H_{24}N_4O_4$: N, 12.95. Found; N, 12.78.

1,2-Di-*p*-tolyl-2-methyl-1-propanone (IV) was prepared by the dialkylation of 4,4′-dimethyldesoxybenzoin[17] with freshly prepared potassium *t*-butoxide and methyl iodide. A solution of 0.22 mole of the ketone in 200 ml of benzene was added with vigorous stirring to 23.5 g of potassium dissolved in 300 ml of *t*-butyl alcohol and 80 ml of benzene. The deep orange solution which resulted was refluxed for 2 hr and 0.60 mole of methyl iodide was added. The reaction mixture was stirred overnight and then cooled in an ice–water bath. A rapid filtration of the cooled mixture removed the precipitated potassium iodide. The organic filtrate was hydrolyzed by the dropwise addition of cold water and the product layer was washed with a saturated saline solution. The organic phase was dried over sodium sulfate, concentrated under vacuum, and distilled. The fraction boiling at 142–144° (0.3 mm) (81% yield) was found to be chromatographically pure. Infrared analysis revealed a single conjugated carbonyl at 1670 cm^{-1}.

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.98. Found: C, 85.58; H, 8.17.

General Procedure for Indene Synthesis.—The material (5–15 g) to be dehydrated was added in small portions to approximately 100 g of polyphosphoric acid being held at 210–230° in a sand or oil bath. The contents of the three-neck, round-bottom reaction vessel were stirred mechanically under a reflux condensor and the temperature of the acid was raised to 260–280° and held there for 3–4 hr. The dehydration was terminated by cooling the reaction mixture to 100° and pouring it onto a 10-volume excess of ice and water. The product was extracted into an ether–benzene layer. The aqueous phase was then neutralized with 40% potassium hydroxide solution and re-extracted with ether and benzene.

The combined organic extracts were washed with sodium carbonate solution until neutral, dried over sodium sulfate, filtered, and concentrated under vacuum. The indenes could usually be isolated by addition of cold methanol to the concentrated organic phase which induced the precipitation of the hydrocarbons. In the cases in which this technique failed, the indenes could be separated by preparative gas chromatography.

When 2-methyl-3-phenylidene[11] was treated by this procedure it was converted into a mixture of 63% 2-phenyl-3-methylindene and 32% unreacted starting material after 3.5 hr of contact. Indene separation was accomplished on the Apiezon N column under the conditions described.

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[17] R. Stierlin, *Ber.*, **22**, 376 (1889).

Cleavage Reaction of 2-Butenyloxy Derivatives with Potassium *t*-Butoxide

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Received July 12, 1965

The base treatment of β,γ-unsaturated systems (I) (ethers, amines, sulfides, sulfoxides, sulfones, esters, ketones, and nitriles) has been reported to result in partial or complete isomerization to the corresponding α,β-unsaturated systems (II) or elimination and in some cases both types of reactions.

$$\underset{\text{I}}{R{-}CH{=}CH{-}CH_2{-}X} \qquad \underset{\text{II}}{RCH_2{-}CH{=}CH{-}X}$$

Virtually complete isomerization of the unsubstituted β,γ isomers I [R = H; X = $-OC_6H_5$, $-S-C_6H_{13}$, $-N(CH_3)_2$] to the corresponding α,β isomers occurred readily with potassium *t*-butoxide in DMSO or DME[1] (1,2-dimethoxyethane). In addition, similar observations were noted for unsubstituted β,γ-unsaturated ethers using alkoxide catalysts without a solvent.[2] It has also been known for some time that the base-induced equilibria between I (R = H; X = –CN, –COOH, CO_2^-, $-COOC_2H_5$, $O{=}\overset{|}{C}CH_3$) and the corresponding α,β isomers II predominantly favor the latter.[3] However, a shift in the equilibria to favor the β,γ isomers was noted when the analogous γ-substituted compounds I (R = CH_3 or alkyl) were subjected to base treatment.[3] More recently, O'Connor and Lyness[4] similarly observed a predominance of the β,γ isomer in a study of the base-catalyzed equilibria of unsaturated sulfur derivatives I (R = alkyl; X = $-SOCH_3$, $-SO_2CH_3$). In the case of the γ-substituted sulfide I (R = CH_3 or alkyl; X = $-SOCH_3$), both equilibration to a mixture of the β,γ isomer I (34%) and the α,β isomer II (66%) and 1,4-diene elimination was observed.[4b] The reactions of cyclic butadiene sulfone[5] and 1-O-heptadec-2-enyl-2,3-O-isopropylidene glycerol ether[6] with base have only been reported to involve diene elimination.

Among the numerous isomerization studies of unsaturated systems described above, only one involved a study of the reaction of a γ-substituted β,γ-unsaturated ether with base. In this report, diene elimination was observed from the alkenyl glycerol ether; however, there was no indication of whether or not isomerization had occurred.[6] As part of our continuing studies of the chemistry of ortho esters, we investigated the base-catalyzed isomerization reaction of tri-2-butenyl orthoformate (III) and also that of a related system, phenyl-2-butenyl ether (IV). The reactions of III and IV with catalytic or molar quantities of potas-

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[1] (a) C. C. Price and W. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1773 (1961); (b) C. C. Price and W. H. Snyder, *Tetrahedron Letters*, **No. 2**, 69 (1962); (c) C. C. Price and W. H. Snyder, *J. Org. Chem.*, **27**, 4639 (1962).

[2] T. L. Prosser, *J. Am. Chem. Soc.*, **83**, 1701 (1961).

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 562.

[4] (a) D. E. O'Connor and W. I. Lyness, *J. Am. Chem. Soc.*, **85**, 3044 (1963); (b) D. E. O'Connor and W. I. Lyness, *ibid.*, **86**, 3840 (1964).

[5] T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *ibid.*, **85**, 2739 (1965).

[6] J. Cunningham and R. Gigg, *J. Chem. Soc.*, 2968 (1965).

sium *t*-butoxide without a solvent or in dimethyl sulfoxide (DMSO) resulted only in butadiene elimination (eq 1 and 2) and in neither case was any isomerization to the α,β-unsaturated isomer observed.

$$\mathrm{HC(OCH_2CH{=}CHCH_3)_3} + t\text{-BuOK} \longrightarrow \underset{\mathrm{III}}{\mathrm{CH_2{=}CHCH{=}CH_2}} + \mathrm{CH_3CH{=}CHCH_2OH} + \mathrm{HCOOK} + t\text{-BuOH} \quad (1)$$

$$\underset{\mathrm{IV}}{\mathrm{C_6H_5OCH_2CH{=}CHCH_3}} + t\text{-BuOK} \longrightarrow \mathrm{CH_2{=}CH{-}CH{=}CH_2} + \mathrm{C_6H_5OK} + t\text{-BuOH} \quad (2)$$

The total absence of isomerization in these 2-butenyloxy derivatives was unexpected since all other γ-substituted β,γ-unsaturated systems reported exist in equilibria with varying concentrations of the α,β-unsaturated isomers. Even in the case of the alkenylmethyl sulfide previously described, where elimination was the predominant reaction path, a rapidly established equilibrium between the unsaturated isomeric forms was still observed. This is apparently the first report of the absence of isomerization in a β,γ-unsaturated system such as I under basic conditions.

Elimination reactions of a variety of aliphatic functional derivatives with potassium *t*-butoxide in DMSO have been previously reported[4b,5,7] Further studies have established that the elimination reactions occur by an E2 mechanism.[8] The postulated mechanism for the base-catalyzed isomerization of β,γ- to α,β-unsaturated compounds has been considered to involve a free or complexed carbanion intermediate.[1a,9] Generally, rate enhancements of 10^3 to 10^7 are observed for base-catalyzed reactions in DMSO relative to alcoholic solvents[10] or DME.[1a] In a study of the relative rates of reaction of phenyl-2-butenyl ether (IV) with potassium *t*-butoxide in DMSO and DME at 25°, the rate of elimination was 38 times faster in DMSO[11] (see Table I). Although a carbanion process (Chart I) cannot be excluded as a possible mechanism in this reaction, this path is considered unlikely based upon the absence of isomerization. The E2 mechanism (Chart II) is considered to be a more plausible path. The relatively small rate enhancement observed in DMSO might be considered evidence for the E2 process since charge separation in the transition state would be minimal and large differences in solvent dielectric constant would not be substantially reflected in the rate.

TABLE I

RELATIVE RATES OF 1,3-BUTADIENE ELIMINATION AT 25°
(0.66 *M* *t*-BuOK, 0.66 *M* phenyl-2-butenyl ether)

Reaction time, min	Moles of butadiene × 10⁴ DMSO	Moles of butadiene × 10⁴ DME
5	6.84	1.2
30	13	1.42
180	32.9	4.3
420	32.7	8.1

CHART I

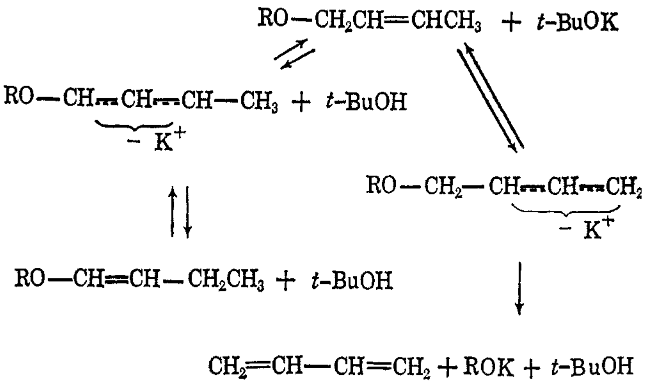
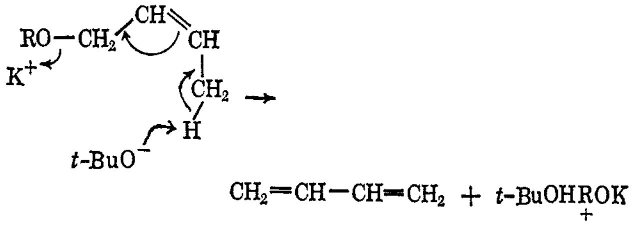


CHART II



R = $\mathrm{C_6H_5}$- or $\mathrm{-CH(OCH_2CH{=}CHCH_3)_2}$

It is interesting to note that the reaction of phenyl-*n*-butyl ether with potassium *t*-butoxide in DMSO at 55° was reported to give a 17.6% yield of isomeric 2-butenes in 169 hr.[7a] We have found that phenyl-2-butenyl ether under comparable conditions at 55° gave a 17.6% yield of butadiene in 4 min. Therefore, elimination from the unsaturated ether occurred 10^3 times faster than from the saturated ether. This rate enhancement is consistent with an E2 mechanism for both systems. Among the factors which affect the rate of these eliminations, one must consider both the relative energy requirements for incipient olefin formation and for departure of the leaving group in the transition state. The fact that both of these factors are important is apparent since di-*n*-butyl ether[7a] and di-2-butenyl formal[12] do not undergo elimination under these conditions, while the hepta-2-decenyl glycerol ether[6] and tri-2-butenyl orthoformate undergo rapid elimination.

Ortho esters of carboxylic acid are normally only decomposed to the corresponding acids and alcohols in aqueous acid.[13] However, these same ortho esters are generally very stable under basic conditions.[14] The base decomposition of tri-2-butenyl orthoformate is indeed an unusual and unexpected reaction for this class of ortho esters.

Further studies are in progress in an attempt to distinguish between the mechanistic possibilities presented.

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(7) (a) T. J. Wallace, J. R. Hofmann, and A. Schriesheim, *Nature*, **199**, 1287 (1963); (b) T. J. Wallace, H. Pobiner, J. E. Hofmann, and A. Schriesheim, *Proc. Chem. Soc.*, 137 (1963); (c) J. E. Hofmann, T. J. Wallace, P. A. Argabright, and A. Schriesheim, *Chem. Ind.* (London), 1243 (1963).

(8) J. E. Hofmann, T. J. Wallace, and A. Schriesheim, *J. Am. Chem. Soc.*, **86**, 1561 (1964).

(9) C. D. Broaddus, *ibid.*, **87**, 3706 (1965).

(10) A. J. Parker, *Advan. Org. Chem.*, **5**, 9–12 (1965).

(11) A comparison of the rate data in Table I indicates a 17% yield of butadiene formed in 11 min in DMSO and in 420 min in DME, corresponding to a rate 38 times faster in DMSO.

(12) Unpublished data from our laboratory.

(13) See, J. Hine, "Physical Organic Chemistry," 1st ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 190.

(14) Silico ortho esters have been demonstrated to decompose under basic conditions.[15] Recently, orthoformate decomposition has been observed with butyl lithium.[16]

(15) H. W. Post, "Chemistry of Aliphatic Orthoesters," Reinhold Publishing Corp., New York, N. Y., 1943, p 130.

(16) K. D. Berlin and B. S. Rathore, *Tetrahedron Letters*, **No. 37**, 2547 (1964).

Experimental Section

The melting points were taken on a Thomas–Hoover capillary melting point apparatus and were corrected. Analyses for the rate study were obtained on an F & M Model 720 vapor fractometer using a 6-ft 10% Squalane on Haloport column (U column). All other vapor chromatographic analyses were determined on a 6-ft Carbowax 1500 on Teflon column using a Perkin-Elmer vapor fractometer. The infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer.

Materials.—Phenyl-2-butenyl ether was prepared according to the method of Goering and Jacobson.[17] Tri-2-butenyl orthoformate was prepared by the exchange reaction of triethyl orthoformate and but-2-en-1-ol, bp 138° (11 mm), $n^{20}D$ 1.4543. Dimethyl sulfoxide and 1,2-dimethoxyethane were distilled over Linde Molecular Sieve 13X before use in the rate study. Potassium *t*-butoxide was purchased from City Chemical Corp.

Rate Study. A. Preparation of Reaction Mixture.—A solution containing 0.6862 (0.00463 mole) of phenyl-2-butenyl ether and 0.324 g of pentane (internal standard) in 7 ml of the desired solvent (DMSO or DME) was prepared and purged with nitrogen. The vial was cooled in Dry Ice and 0.5120 g (0.00457 mole) of potassium *t*-butoxide was added to the solution and the solution purged with nitrogen again before sealing with a serum cap. Each solution was 0.66 *M* in reactant and base. The vial was then placed in a constant-temperature bath, stirred by means of a magnetic stirrer, and then sampled and analyzed.

B. Analyses of Reaction Mixtures.—Aliquots (0.2 ml) were withdrawn at the requisite time and injected in a serum cap sealed vial containing 3 ml of water and 1 ml of isooctane. This sample was cooled in Dry Ice and the hydrocarbon layer was sampled for butadiene by gas chromatography with a pre-cooled syringe. The lower boiling components were analyzed with a U column on the F & M Model 720 vapor fractometer at 50° and the higher boiling components analyzed by programming to 170° at 30°/min. The yield of butadiene was calculated from the gc area of pentane (internal standard) and the gc area of butadiene.

Reaction of 2-Butenyl Phenyl Ether with Potassium *t*-Butoxide.—A suspension of 11.2 g (0.1 mole) of potassium *t*-butoxide in 14.8 g (0.1 mole) of 2-butenyl phenyl ether was heated during 1 hr from 25 to 126° and the gas evolved was passed through a bromine solution in carbon tetrachloride (36 g in 35 ml). After the 1-hr heating period, the gas evolution ceased and the reaction mixture was diluted with 50 ml of water. An organic layer formed which was separated, dried ($MgSO_4$), and filtered. This liquid (6.4 g, 0.043 mole) was shown by infrared analysis to be unreacted starting ether. An additional 1.0 g (0.007 mole) of starting material was obtained by ether extraction of the aqueous reaction mixture. Acidification of the quenched reaction mixture with 3 *N* HCl and subsequent ether extraction provided 3.3 g (0.035 mole) of phenol identified as its tribromo derivative (mp 92–94°).

Evaporation of the bromine–carbon tetrachloride solution provided 16 g (0.043 mole) of a mixture of the isomeric 1,2,3,4-tetrabromobutane, mp 115–118° and 37–40° (isomers, lit.[18] mp 116–117° and 38°). The gaseous product was collected as a liquid at low temperature in one experiment and its infrared spectrum in carbon tetrachloride was identical with the spectrum of 1,3-butadiene in the same solvent. In addition this gaseous product formed a solid upon heating with maleic anhydride in benzene, mp 97–99.5° (1,3-butadiene–maleic anhydride adduct, lit.[19] mp 101–103°).

Reaction of 2-Butenyl Orthoformate with Potassium *t*-Butoxide.—A suspension of 11.2 g (0.1 mole) of potassium-*t*-butoxide in 22.6 g (0.1 mole) of 2-butenyl orthoformate was heated during 2 hr from 25 to 95° and the gas evolved was bubbled through a bromine solution in carbon tetrachloride (20 g in 35 ml). Evaporation of the bromine–carbon tetrachloride solution gave 14 g (0.037 mole) of a mixture of the isomeric 1,2,3,4-tetrabromobutanes. Infrared analysis of the gaseous product from this reaction proved its identity as 1,3-butadiene. The reaction mixture was distilled at atmospheric pressure to give several liquid fractions. These fractions upon glpc analysis showed the following components present: 2-buten-1-ol (5.0 g, 0.069 mole), 1,3-butadiene (0.87 g, 0.016 mole), *t*-butyl alcohol (3.65 g, 0.049 mole), unknown liquid (0.86 g). The residue which remained in the flask was suspended in 35 ml of a 10% solution of anydrous hydrogen chloride in diethyl ether and stirred at 25° for 1 hr. The ether layer was separated from the solid and evaporated to 4.36 g of a viscous liquid, from which 0.47 g (0.01 mole) of formic acid was isolated. The remaining 3.89 g remained unidentified. Infrared analysis showed the unknown liquid to be a carbonyl compound.

Cleavage Reaction Using Potassium *t*-Butoxide in DMSO. A. 2-Butenyl Phenyl Ether.—A solution of 11.9 g (0.017 mole) of potassium *t*-butoxide and 15.9 g (0.107 mole) of 2-butenyl phenyl ether in 75 ml of DMSO was stirred at 25° for 2 hr. This system was connected to a trap containing a bromine solution in carbon tetrachloride (20 g in 35 ml). Very little gassing occurred at this temperature but heating the solution at 70° for 1 hr produced vigorous gas evolution. The solution was stirred an additional 16 hr at 25° and was then quenched with an equal volume of water. Evaporation of the bromine–carbon tetrachloride solution gave 15 g (0.040 mole) of a mixture of the isomeric 1,2,3,4-tetrabromobutanes. Extraction of the aqueous solution with ether provided 7.2 g (0.048 mole) of starting ether. Acidification of the aqueous phase with 3 *N* HCl and subsequent ether extraction gave 3.6 g (0.038 mole) phenol (phenylurethan derivative, mp 123–124°, lit.[20] mp 126°).

B. 2-Butenyl Orthoformate.—A solution of 11.2 g (0.10 mole) of potassium-*t*-butoxide and 22.6 g (0.10 mole) of ortho ester in 75 ml of DMSO was stirred at 25° for 10 min. This system was connected to a bromine trap as described above. There was very little gas evolution at 25° but when the reaction mixture was heated at 70° considerable gassing was observed. After 2 hr at this temperature the reaction was stopped. Dilution of the reaction mixture provided no organic layer. Evaporation of the bromine solution gave 6.6 g (0.017 mole) of a mixture of the isomeric 1,2,3,4-tetrabromobutanes. Both 2-buten-1-ol and *t*-butyl alcohol were qualitatively identified as additional products of this reaction by distillation of the reaction mixture before quenching it with water. Quantitative determination of the latter compounds and formic acid was interfered with by the presence of DMSO.

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[17] H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958).

[18] R. A. Jacobson, *ibid.*, **54**, 1545 (1932).

[19] M. C. Klotetzel, *Org. Reactions*, **IV**, 41 (1949).

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Tautomerism in N-Acetyl Sulfonamides. A Clarification

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Received March 21, 1966

Ishidate and Momose[1] have reported the isolation of two diacetyl-4-(aminomethyl)benzenesulfonamides and assumed the products to be the amide–imide tautomers, $AcNHCH_2C_6H_4SO_2NHAc$ and $AcNHCH_2C_6H_4$-$SO(OH){=}NAc$. This conclusion was based on the interconversion of the two products A and B as shown in Scheme I.

SCHEME I