

A sample of ozonolysis product obtained in this manner by the reduction with hydrogen at 1 atm. gave only a small amount (1% yield) of non-crystalline derivative with *o*-phenylenediamine.

Poly-1,7-octadiyne and Poly-1,8-nonadiyne.—The polymerization of 9.3 g. of 1,7-octadiyne with the 3:1 aluminum triisobutyl-titanium tetrachloride catalyst afforded 7.78 g. (83.6%) of a light colored polymer which was 48.7% soluble in a continuous extraction with refluxing xylene. The soluble portion had an inherent viscosity of 0.063. The infrared spectrum of the soluble portion of this polymer showed an infrared absorption maximum at 1605 cm^{-1} and

no maxima characteristic of an acetylenic group. No absorption was shown in the visible region.

The polymerization of 10 g. of 1,8-nonadiyne with the same catalyst gave 9.2 g. (92%) of a light colored polymer which was 22% soluble in a continuous extraction with xylene. The soluble portion had an inherent viscosity of 0.067. The infrared spectrum of the soluble portion showed maxima at 3295 and 2120 cm^{-1} , characteristic of the acetylenic group as well as a maximum at 1605 cm^{-1} (C=C conj.). A quantitative comparison of the absorption for the acetylenic maxima of the polymer compared with the monomer showed that 25–30% of the monomer units had polymerized through only one of the acetylenic groups.

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO., WILMINGTON, DEL.]

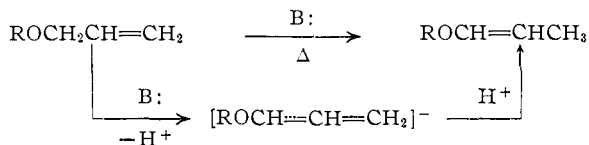
The Rearrangement of Allyl Ethers to Propenyl Ethers

By T. J. PROSSER

RECEIVED OCTOBER 18, 1960

Several mono- and polyfunctional allyl ethers have been rearranged to the corresponding propenyl ethers by treatment at 150–175° in the presence of a basic catalyst. The rearrangement reaction is stereospecific, yielding 95–100% *cis*-propenyl ether. A catalyst deactivation effect is observed with ultimate degree of rearrangement being a function of initial catalyst concentration but not of temperature. The rearrangement reaction affords a convenient preparative procedure for propenyl ethers.

The base-catalyzed rearrangement of an allyl ether to a propenyl ether apparently represents a further example of that group of reactions classified as true, three-carbon prototropic shifts.¹



The isomerization of certain allylic ethers has been mentioned briefly in the literature. Vinyl allyl ether is converted to vinyl propenyl ether by treatment with metallic sodium or alkoxide ion.² Partial rearrangement of 1-allyloxy-2-propanol is reported by refluxing with potassium hydroxide, and allyloxy end-group unsaturation in polypropylene glycol is isomerized to propenyloxy unsaturation at 100° under basic conditions.³ Also

(1) A true, three-carbon prototropic system is defined as one in which the nature of the activating groups is such that covalency changes beyond the limits of the three-carbon system itself are structurally excluded, *i.e.*, the negative charge on the allylic anion is located within the limits of the system itself (J. W. Baker, "Tautomerism," D. Van Nostrand Co., Inc., New York, N. Y., 1934, p. 80). That oxygen does not participate in resonance stabilization in the prototropic rearrangement of an allyl ether to a propenyl ether is suggested by the fact that allyl ethers do not rearrange under conditions which readily isomerize allyl sulfides to propenyl sulfides [(a) D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952); D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956)]. This difference is attributed to the ability of sulfur to expand its electron shell to a d-orbital and thus participate in resonance stabilization of the intermediate allylic carbanion. Other examples of three-carbon prototropy in the above sense are the base-catalyzed rearrangements of quaternary ammonium-substituted propylene [(b) C. K. Ingold and E. Rothstein, *J. Chem. Soc.*, **8** (1929): 1666 (1931)], the isomerization of olefinic hydrocarbons [(c) W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 387 (1960)], and the migration of double bonds in the Varrentrapp reaction [(d) R. G. Ackman, P. Linstead, B. J. Wakefield and B. C. L. Weedon, *Tetrahedron*, **8**, 221 (1960)].

(2) R. Paul, G. Roy, M. Fluchaire and G. Collardeau, *Bull. soc. chim. France*, 121 (1950); W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

(3) D. M. Simons and J. J. Verbanc, *J. Polymer Sci.*, **44**, 303 (1960).

3-butoxy-2-methylpropene has been rearranged to 1-butoxy-2-methylpropene by treatment with potassium amide in liquid ammonia.⁴ A somewhat obscure example of the rearrangement is found in the conversion of bis-(1,3-diphenylallyl) ether to the corresponding dipropenyl ether by treatment with refluxing sodium ethoxide.⁵ Here, the isomerization could be ascribed entirely to the mobility of the 1,3-diphenylpropene systems.⁶

In the present work, a variety of mono- and polyfunctional allyl ethers have been rearranged to the corresponding propenyl ethers. Table I summarizes reaction conditions and results. In general, the reaction proceeds readily at 150–175° in the presence of 5% of a basic catalyst. Potassium *t*-butoxide was an effective catalyst in all cases, whereas sodium methoxide showed appreciable activity toward pentaerythritol tri- and tetraallyl ethers only. These differences probably are due to the fact that potassium *t*-butoxide is the more soluble catalyst and is a stronger base. The rearrangement of pentaerythritol ethers occurred also in the presence of sodium or potassium hydroxides.

Certain color changes are observed during the reaction. A yellow mixture was obtained upon addition of catalyst to the substrate. When the mixture was heated, the yellow color changed to orange or orange-red. The final product was usually light yellow. Such color changes are probably indicative of a process involving a carbanion intermediate^{4,7} as in eq. 1.

Rearrangements were followed qualitatively by inspection of the infrared spectra of reaction samples. The major spectral changes are the appearance of a sharp, very intense band at 5.98 μ , accompanied by strong, broad absorption at about

(4) A. J. Birch, *J. Chem. Soc.*, 1642 (1947).

(5) C. W. Shoppee, *ibid.*, 2567 (1928).

(6) C. K. Ingold and C. W. Shoppee, *ibid.*, 447 (1929).

(7) C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.*, **73**, 1437 (1951).

TABLE I
 REARRANGEMENT OF ALLYL ETHERS TO PROPENYL ETHERS

Ether rearranged	Rearrangement conditions			Conversion to propenyl ether, %		Maximum <i>trans</i> -propenyl ether content, %	
	Catalyst, wt. % concn.	Temp., °C.	Time, hr. ^a	Infrared	Chemical		
Cetyl allyl ether	<i>t</i> -BuOK	2	150	48	84.0
	<i>t</i> -BuOK	5	150	6	>96	96.3 ^b	Nil
	<i>t</i> -BuOK	2	175	24	88.0	92.3 ^b	..
	<i>t</i> -BuOK	5	175	6	>96	...	Nil
	MeONa	5	175	54	N.R. ^c
1,4-Diallyloxybutane	<i>t</i> -BuOK	2	150	48	N.R. ^c
	<i>t</i> -BuOK	5	150	48	>98.8	94.0 ^d	2.8
	<i>t</i> -BuOK	2	175	48	10
	<i>t</i> -BuOK	5	175	6	>98.8	99.0 ^d	1.8
	MeONa	5	175	163	18.5
4-Allyloxy-1-butanol	<i>t</i> -BuOK	2	150	48	N.R. ^c
	<i>t</i> -BuOK	5	175	48	44.4	35.2 ^b	..
1,5-Diallyloxy-pentane	<i>t</i> -BuOK	2	150	48	17.2
	<i>t</i> -BuOK	5	150	48	>98.7 ^e	94.0 ^d	5.2
	<i>t</i> -BuOK	2	175	48	N.R. ^c
	<i>t</i> -BuOK	5	175	3	86.3
	MeONa	5	175	143	18.5
1,6-Diallyloxyhexane	<i>t</i> -BuOK	5	150	24	13.6
	MeONa	5	175	102	13.0
	<i>t</i> -BuOK	2	150	24	10.5
PE ^f triallyl ether	<i>t</i> -BuOK	5	150	48	41.4	40.9 ^b	..
	<i>t</i> -BuOK	5	175	24	23.2
	<i>t</i> -BuOK	10	175	48	83	79.4 ^b	..
	<i>t</i> -BuOK	15	175	48	86
	MeONa	5	175	52	57.0
	MeONa	5	175	97	55.4
PE tetraallyl ether	<i>t</i> -BuOK	2	150	48	N.R. ^c
PE trimethallyl ether	<i>t</i> -BuOK	5	175	48	88.3
2,2-Dimethyl-5,5-bis-(allyloxymethyl)-1,3-dioxane	<i>t</i> -BuOK	5	175	24	55.3	53.5 ^b	..
3- <i>n</i> -Propoxycyclohexene	<i>t</i> -BuOK	10	150	24	N.R. ^c

^a Represents time of maximum observed conversion; in most cases near maximum conversion was achieved after 5–10 hr. ^b Determined iodometrically by method of S. Siggia and R. L. Edsberg, *Anal. Chem.*, **20**, 762 (1948); starting allyl ethers do not interfere. ^c No reaction; determined qualitatively by infrared analysis. ^d Determined by acid hydrolysis and analysis of the liberated propionaldehyde as its 2,4-DNP derivative [S. Siggia, "Quantitative Organic Analysis Via Functional Groups," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1954, p. 31]; starting allyl ethers gave negligible blank values. ^e In a similar experiment a 94.9% yield of 97% rearranged material was obtained. ^f Pentaerythritol.

13.8 μ . These bands correspond to propenyl C=C stretching and to *cis*-propenyl, C—H out-of-plane bending, respectively.⁸ A corresponding decrease in absorption at 6.07 μ (allyl C=C stretching) and at about 10.8 μ (allyl C—H out-of-plane bending) also was observed. Less prominent changes were noted in the 7 to 8 μ , methyl and methylene region.

The degree of rearrangement was determined quantitatively by measuring the decrease in terminal methylene (*i.e.*, allyl group) by near-infrared spectrophotometry. Absorption at 1.633 or 2.113 μ was appropriate for this purpose. In several cases the infrared values were corroborated by chemical analyses involving either acid hydrolysis and determination of the liberated propionaldehyde or iodometry.

Product identification was based on infrared data, acid hydrolysis to propionaldehyde and the parent alcohol, and oxidation to acetic acid.

A catalyst deactivation effect of unknown mechanism is observed in the rearrangement reaction. Thus, near-maximum, but not necessarily complete, conversions to propenyl ethers were

usually observed after reaction periods of five to ten hours with only little further rearrangement being obtained upon extended heating. The ultimate degree of rearrangement in a given system depends upon initial catalyst concentration but is essentially independent of temperature. Therefore the observed termination is not an indication of an equilibrium condition. The effect is illustrated in Fig. 1 for the isomerization of 1,5-diallyloxy-pentane. The magnitude of the catalyst deactivation effect appears to depend upon functionality, cetyl allyl ether being affected less than the di- and trifunctional ethers tested. The deactivation effect has been noted previously in allyl ether rearrangements but was interpreted as an indication of an equilibrium reaction.⁸

The potential value of the rearrangement reaction as a preparative procedure was demonstrated by treatment of 1,5-diallyloxy-pentane with 5% potassium *t*-butoxide at 150° for 24 hours. The product, 97% rearranged, was recovered in 94.9% yield.

The isomerization is essentially stereospecific, giving the *cis*-propenyl ether. The infrared spectra of those ethers where rearrangement proceeded to completion showed negligible absorption in the

(8) G. T. Dege, R. L. Harris and J. S. McKenzie, *J. Am. Chem. Soc.*, **81**, 3374 (1959).

TABLE II
 ALLYL ETHERS

Ether	Boiling point		n_{20}^D	Br number		Purity, % ^a
	°C.	Mm.		Found	Calcd.	
PE ^b tetraallyl ether	152-153.9 ^c	9.5-10	1.4602 ^c	199	215.7	90 ^d
PE triallyl ether	152-152.5	9.5-10	1.4650	185	187.1	100
PE trimethylallyl ether ^e	176	10	1.4665	164	160.7	...
1,4-Diallyloxybutane	91-93.2 ^f	14.5-15	1.4370	187	187.8	99.9
4-Allyloxybutanol-1 ^g	99-104	19.5	1.4434	113	122.7	...
1,5-Diallyloxy-pentane	104-106.5	13.0	1.4414	174	173.5	97.5
1,6-Diallyloxyhexane	115.5-116.3	12-12.5	1.4435	156	161.2	95.2
Cetyl allyl ether	185-187 ^h	9	...	56	56.6	...
3- <i>n</i> -Propoxycyclohexene ⁱ	85-86.5	41	1.4530	112	114.0	...

^a By vapor phase chromatography. ^b Pentaerythritol. ^c Reported^{14a} b.p. 124-125° (1 mm.), n_{20}^D 1.4595. ^d Contained 10% pentaerythritol triallyl ether. ^e Hydroxyl content: calcd. 5.70, found 5.4. ^f Reported: b.p. 84-87° (10 mm.) [P. Kurtz, *Ann.*, **572**, 23 (1951)]. ^g Hydroxyl content: calcd. 13.06, found 11.5. ^h Reported: b.p. 186-189° (11 mm.) [C. M. Hill, L. Haynes, D. E. Simmons and M. E. Hill, *J. Am. Chem. Soc.*, **75**, 5408 (1953)]. ⁱ *Anal.* Calcd. for C₉H₁₆O: C, 77.09; H, 11.50. Found: C, 76.73; H, 11.52.

The physical constants and analyses of all of the allyl ethers used in this work are listed in Table II.

Preparation of 2,2-Dimethyl-5,5-bis-(allyloxymethyl)-1,3-dioxane.—A mixture of 30 g. (0.14 mole) of pentaerythritol diallyl ether,¹⁸ 100 ml. of acetone, 5 drops of concd. sulfuric acid and a small amount of Molecular Sieve drying agent was heated at reflux for 20 hr. The mixture was neutralized with calcium hydroxide, filtered and the filtrate concentrated, giving 29.5 g. of crude product containing residual hydroxyl. Fractionation of the product gave a main fraction weighing 18.5 g. [b.p. 139-142° (16-16.5 mm.), n_{20}^D 1.4570, Br no. 124 (theory 124.7)], representing a 52% yield of ketal.

Alkoxide Catalysts.—Potassium *t*-butoxide was prepared by treatment of excess *t*-butyl alcohol (purified by distillation from metallic sodium) with potassium metal at reflux temperature. The product was dried at 60° *in vacuo* and used without further purification. Commercial sodium methoxide (Matheson Coleman & Bell) was employed as received.

Rearrangement Reactions.—Rearrangements were effected without solvent under nitrogen in capped, heavy-walled vials employing 5-10 g. of the allyl ether. Samples were isolated with a hypodermic syringe and neutralized in ether solution with anhydrous Dowex 50 prior to analysis. Some reactions were carried out in an apparatus allowing isolation of samples *via* vacuum distillation through a short, unpacked column. Sample fractionation was considered

(18) Prepared similarly to the triallyl ether: for diallylpentaerythritol, b.p. 164.5-165° (9.5 mm.), n_{20}^D 1.4722, Br no. 149 (calcd. 147.8), hydroxyl content 15.4% (calcd. 15.73%); reported: b.p. 120° (1 mm.), n_{20}^D 1.4729 [R. Evans and J. A. Gallagher, *J. Am. Chem. Soc.*, **75**, 1248 (1953)].

unlikely because of the proximity of the boiling points of corresponding allyl and propenyl ethers.

Heterogeneous reaction mixtures were encountered in all cases. Potassium *t*-butoxide was appreciably soluble in all of the allyl ethers tested while sodium methoxide appeared essentially insoluble. Reaction mixtures were not agitated but were thoroughly mixed during intermittent sampling.

Hydrolysis of Rearrangement Products.—Samples of completely rearranged 1,4-diallyloxybutane and 1,5-diallyloxy-pentane were treated with methanol in the presence of Dowex 50 acidic exchange resin at room temperature for 24 hr. After filtration and removal of methanol the products were identified as 1,4-butanediol and 1,5-pentanediol, respectively, by comparison of their infrared spectra with those of the authentic diols.

Hydrolysis of various rearrangement products with 2,4-dinitrophenylhydrazine (DNP) reagent gave derivatives identified as propionaldehyde 2,4-DNP. Thus, partially rearranged pentaerythritol triallyl ether gave a derivative which, after recrystallization from ethanol, melted at 155-156.5° (reported¹⁹ m.p. 155°) and which did not depress the melting point of an authentic sample of propionaldehyde 2,4-DNP.

Oxidation of Rearranged Pentaerythritol Triallyl Ether.—A 10.4-g. (0.04 mole) portion of partially rearranged material in 100 ml. of water was treated with 55 g. (0.35 mole) of potassium permanganate over a 1-hr. period. The product was filtered and the filtrate concentrated and acidified. Continuous ether extraction gave a product identified as acetic acid by infrared analysis. Neutralization with sodium hydroxide and drying gave a white solid identified as sodium acetate by its X-ray diffraction pattern.

(19) O. L. Brady and G. V. Elmslie, *Analyst*, **51**, 78 (1926).