[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ROHM & HAAS CO.]

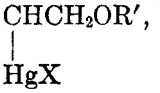
Homogeneous Metal Salt Catalysis in Organic Reactions. III. The Preparation of Allyl Ethers by Allyl Transfer Reactions[1,2]

WARREN H. WATANABE, LAWRENCE E. CONLON,[3] AND JESSE C. H. HWA

Received May 16, 1958

There is described a reaction between an alcohol and an allyl ether or allyl alcohol which provides a simple one-step synthesis of allyl ethers. The catalysts used are mercuric salts of strong acids, or combinations of mercuric salts such as mercuric acetate with strong acids. Several modifications of this reaction are described; yields range from about 50% to near-quantitative. A possible reaction scheme is proposed.

In a recent publication we described the reaction of a vinyl ether, $CH_2{=}CH{-}OR$, with an alcohol, R′OH, in the presence of a weak acid salt of mercury to effect a vinyl transfer, leading to a new vinyl ether, $CH_2{=}CH{-}OR'$, and ROH. It was postulated that this reaction proceeded through a symmetrical intermediate, labile to weak acid, of the form  $\begin{matrix}RO\\R'O\end{matrix}\!\!>\!CHCH_2HgX$, which could break down either to starting material or to products, thus explaining the equilibrium character of this reaction.

A second type of symmetrical intermediate, closely analogous to that above, but one which is derived from the allyl ether system, was then conceived. This postulated intermediate was  $ROCH_2\text{-}\underset{\displaystyle HgX}{\underset{|}{C}}HCH_2OR'$, expected to be labile to strong acid, which would make possible a reaction of allyl transfer. We now report the successful confirmation of this prediction by the discovery of novel methods of preparation of allyl ethers.

The reactions studied were the following:

$$CH_2{=}CHCH_2OR + R'OH \rightleftarrows CH_2{=}CHCH_2OR' + ROH \quad (1)$$

$$CH_2{=}CHCH_2OH + ROH \longrightarrow CH_2{=}CHCH_2OR + H_2O \quad (2)$$

A third reaction,

$$(CH_2{=}CHCH_2)_2O + 2ROH \longrightarrow 2CH_2{=}CHCH_2OR + H_2O \quad (3)$$

was also studied separately since allyl ether is readily available and is a convenient source of allyl goups. In detail, it is most probably a combination of the first two reactions. Thus it may proceed by formation first of the desired alkyl allyl ether and allyl alcohol, then by reaction of allyl alcohol as in (2).

Catalysts. For the three reactions, certain mercuric salts of strong acids, or mercuric salts in the presence of strong acids, were specific catalysts. No other inorganic salts that were tested, either in the presence or absence of strong acid, nor strong acid alone, proved to have catalytic activity when used at the concentrations at which the mercuric salts were effective. Neither reaction (1) nor the modification (3) have hitherto been reported in the literature. Reaction (2), however, is a known method for the preparation of allyl ether,[4] but large amounts of strong acids are required; and in the one reported case in which a metal was used (cuprous chloride, with hydrochloric acid, ammonium chloride, and copper metal[5]), the concentration of catalyst used was greater than that required of the mercuric salts. Thus the cuprous salt was used at about 0.2 mole per mole of allyl alcohol, whereas in this work mercuric salt on the order of 0.01–0.05 mole per mole of allyl compound was sufficient. Since in reactions (2) and (3) inactivation of catalyst through reduction to metallic mercury occurred rapidly, this amount was usually added in several increments.

A survey of a variety of mercuric salt or mercuric salt-acid combinations showed mercuric acetate-boron trifluoride etherate in equimolar combination to give the cleanest reaction and best yields. This combination was therefore used as our catalyst of choice throughout the reaction study. Interestingly, mercuric bromide or mercuric phosphate, although salts of strong acids, were not found to be active.

Reaction Conditions. Reaction (1) was effected simply by mixing the reactants, adding catalyst, and distilling off the new allyl ether. This technique, is, however, highly restricted, since most of the alkyl allyl ethers with alkyl groups containing more than four carbon atoms have boiling points very close to those of their parent alcohols, and separation of the allyl ether from the alcohol by distillation is exceedingly difficult. When this method is possible, however, the yield is high.

Reactions (2) and (3) avoid this limitation, since they may be driven to completion either by

---

[1] For the previous paper in this series, see W. H. Watanabe, *J. Am. Chem. Soc.*, **79**, 2833 (1957).

[2] Presented at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 15, 1958.

[3] Present address, Shawinigan Resins Corp., Springfield, Mass.

[4] Senderson, *Compt. rend.*, **181**, 699 (1925); E. Moffett, *J. Am. Chem. Soc.*, **56**, 2009 (1934).

[5] P. Kurtz, *Ann.*, **572**, 23 (1951).

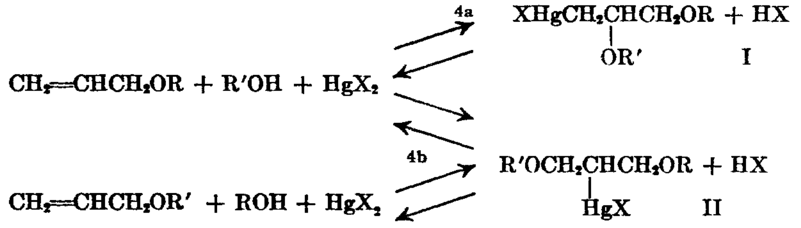
removal of water or by removal of the product if it is lower-boiling than the water-allyl alcohol or water-solvent azeotrope. The general method used was to mix the reactants, add catalyst and a solvent such as benzene, which forms an azeotrope with water, and reflux the mixture through a continuous water separator. The progress of the reaction could be followed by the appearance of water, and increments of catalyst were added when necessary. Yields by this method were on the order of 50%. Typical results are given in Table I.

TABLE I

YIELDS IN THE PREPARATION OF ALLYL ETHERS

Allyl Ether Prepared From	Allylating Agent	Reaction	Yield, %
Methyl alcohol	Allyl ethyl ether	1	85
Methyl alcohol	Allyl alcohol	2	94
Methyl alcohol	Allyl ether	3	67
Allyl alcohol	Allyl alcohol	2	46
n-Butyl alcohol	Allyl alcohol	2	55
n-Octadecyl alcohol	Allyl alcohol	2	47
n-Octadecyl alcohol	Allyl ether	3	71
Cyclohexanol	Allyl alcohol	2	42
Cyclohexanol	Allyl ether	3	58
Benzyl alcohol	Allyl alcohol	2	51

Discussion. While no detailed study of mechanism was undertaken, we consider it probable that, as in the vinyl transfer reaction,[6] these allyl transfer reactions occur by reversible alkoxymercuration. The over-all reactions may be:



$$CH_2{=}CHCH_2OR + R'OH + HgX_2 \underset{}{\overset{4a}{\rightleftharpoons}} \underset{\displaystyle OR'}{XHgCH_2\underset{|}{C}HCH_2OR} + HX \quad \text{I}$$

$$CH_2{=}CHCH_2OR' + ROH + HgX_2 \overset{4b}{\rightleftharpoons} \underset{\displaystyle HgX}{R'OCH_2\underset{|}{C}HCH_2OR} + HX \quad \text{II}$$

The normal direction of addition would be expected to be in the sense of (4a),[7] but such additions are reversible in strong acid[8] and it is necessary only that a small proportion of reaction pass through (II) for allyl transfer to occur.[9] The requirement that strong acid be generated or be added in order to cause allyl transfer is experimentally substantiated by the fact that mercuric acetate alone is ineffective.

Catalyst decomposition, which is marked when R = H, appears to be associated with the formation of acrolein and the reduction of the mercuric salt to free mercury, and thus probably arises from the normal addition intermediate (I).

EXPERIMENTAL

Since some toxic material, presumed to be acrolein, is liberated as a by-product when allyl alcohol or allyl ether are used as allylating agents, it is recommended that these reactions be carried out in a hood.

Catalytic studies. One mole of allyl alcohol was refluxed for a minimum of 1 hr. with 1.0 g. or more of the metal salt through a Dean-Stark continuous water separator. If water collected in the separator, the salt was considered active; of no water formed, the reaction mixture was cooled, 0.5–1.0 g. concentrated sulfuric acid was added, and reflux resumed. If no water formed within 1 hr., the salt was considered inactive. By this test the following salts were inactive: nickel bromide, nickel sulfate, cobalt acetate, cadmium acetate, zinc acetate, manganous chloride, aluminum chloride, and antimony trichloride. Cuprous chloride alone, or in the combination used by Kurtz, was not active at the concentration tested. Mercuric salts which were inactive included mercuric acetate, mercuric benzoate, mercuric bromide, mercuric phosphate, and crystalline mercuric sulfate. Finely ground mercuric sulfate, mercuric acetate plus sulfuric acid, mercuric acetate plus boron trifluoride etherate, and mercuric oxide plus boron trifluoride all showed high activity.

A comparison of mercuric acetate-sulfuric acid and mercuric acetate-boron trifluoride etherate showed the latter to be preferable: in 10 hr., 11.5 g. mercuric acetate with 3 g. of sulfuric acid in 3 moles allyl alcohol gave a 53% conversion to allyl ether and a 97% conversion to metallic mercury; in 3 hr., 11.5 g. mercuric acetate with 3 g. boron trifluoride (20% in ether) in 3 moles allyl alcohol gave a 63% conversion to allyl ether and 82% conversion to metallic mercury.

Preparation of allyl methyl ether. Further catalyst studies. This is an example of reaction (1). To a mixture of 34.4 g. (0.4 mole) allyl ethyl ether and 51.2 g. (1.6 moles) methyl alcohol (boiling point of mixture 56.8°) was added 3.83 g. (*ca.* 3 mole % on ether) mercuric acetate and 1.0 g. (*ca.* 90 mole % on mercury) concentrated sulfuric acid, and the mixture brought to reflux. After 40 min. the vapor temperature had settled at 42.8°. Careful fractionation over a 4-hr. period produced 26.4 g. material, b.p. 42.8–43.5°, n_D^{25} 1.3729, 92% pure by bromine number, giving a yield of 85%. During this distillation the cloudy precipitate originally present in the reaction mixture slowly turned orange-red and remained as such throughout the fractionation. No metallic mercury was formed.

A portion of this product was carefully treated with phosphoric anhydride at room temperature until reaction ceased, and fractionally distilled: b.p. 42–42.3°, n_D^{25} 1.3759 (lit.,[10] b.p. 42.5–43°, n_D^{25} 1.3778–1.3803), d_4^{25} 0.7568.

---

[6] W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

[7] E. Biilmann, *Ber.*, **33**, 1642 (1900); J. Sand and K. A. Hofmann, *Ber.*, **33**, 1359 (1900); K. A. Hofmann and J. Sand, *Ber.*, **33**, 2700 (1900).

[8] R. Adams, F. L. Roman, and W. N. Sperry, *J. Am. Chem. Soc.*, **44**, 1781 (1922); for further references see J. Chatt, *Chem. Revs.*, **48**, 7 (1951).

[9] A splitting of allyl ether to allyl alcohol in the presence of water, nitric acid, and mercuric acetate is implied in the results of R. K. Summerbell, G. Lestina, and H. Waite, *J. Am. Chem. Soc.*, **79**, 234 (1957). This would be the case where R = $CH_2{=}CHCH_2$ and R' = H in the mechanism above.

[10] J. C. Irvine, J. L. A. Macdonald, and C. W. Soutar, *J. Chem. Soc.*, **107**, 337 (1915).

Anal.[11] Calcd. for C_4H_8O: C, 66.63; H, 11.18. Found: C, 66.71; H, 11.22.

Continued distillation of the residue from the original preparation gave a 92% recovery of excess methyl alcohol and a 57% yield of ethyl alcohol.

To an identical mixture of allyl ethyl ether and methyl alcohol, only the mercuric acetate was added and reflux carried out for 1 hr. The boiling point remained at 56.8°. When 1.0 g. sulfuric acid was added, reaction occurred, as in the above example. Another such mixture of allyl ethyl ether and methyl alcohol was refluxed for 2 hr. with 1.0 g. sulfuric acid alone, but no reaction occurred. Reflux for an additional 3 hr. after the addition of 1.0 g. boron trifluoride etherate similarly gave no reaction. Upon addition of 1.9 g. mercuric acetate, reaction occurred, giving allyl methyl ether (n_D^{25} 1.3730) with less than 1 hr. reflux. Reflux of another such mixture of allyl ethyl ether and methanol with 4 g. of 0.72*M* sodium methoxide in methanol for 1.2 hr. gave no reaction.

Examples of reaction (2). Preparation of allyl cyclohexyl ether. A mixture of 99 g. (1 mole) cyclohexanol, 70 g. (1.2 moles) allyl alcohol, 57 g. benzene, 1.5 g. of 45% solution of boron trifluoride in ether, and 4.6 g. (0.04 mole) mercuric acetate was heated under reflux, and the reflux condensate collected in a Dean-Stark water separator. After reflux for 1 hr., 1.6 g. of the boron trifluoride solution and 4 g. mercuric acetate were added and reflux continued for an additional 2 hr. The reaction mixture was then flash-distilled at 0.1 mm. into a receiver cooled with Dry Ice-acetone, and the distillate washed four times with 50 ml. portions of water, dried, and fractionated. An 86.2 g. yield of material, b.p. 81–89°/36–37 mm., found by bromine number analysis to be 84% pure, was obtained. The yield was thus 42% based on cyclohexanol. The crude product was dissolved in an equal volume of benzene, 5 g. boric acid added, and azeotropic distillation carried out until no further water separated out. The pure allyl cyclohexyl ether was then obtained by fractional distillation: b.p. 81–83.5°/38–39 mm., n_D^{25} 1.4483, d_4^{25} 0.8830.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.51; H, 11.49.

By essentially identical procedures *allyl ether* was prepared in 46% yield: b.p. 94–94.8°, n_D^{25} 1.4134, d_4^{25} 0.8027.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.43; H, 10.13.

The same method gave *allyl n-butyl ether*, b.p. 64–65°/120 mm., n_D^{25} 1.4029, d_4^{25} 0.7794 (lit.[12] b.p. 117.8–118°/763 mm., n_D^{20} 1.4057, d_4^{20} 0.7829), in 55% yield.

The same method gave *allyl octadecyl ether* in 47% yield: b.p. 146–153°/0.15–0.20 mm., m.p. 26–27°.

Anal. Calcd. for $C_{21}H_{42}O$: C, 81.21; H, 13.63. Found: C, 81.10; H, 13.62.

Allyl benzyl ether was also prepared in 51% yield by this method: b.p. 71–71.5°/5 mm., n_D^{25} 1.5052, d_4^{25} 0.9548.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.43; H, 8.60.

Example of reaction (3). The preparation of allyl octadecyl ether. A solution of 135 g. (0.5 mole) *n*-octadecyl alcohol in 85 g. benzene was prepared and in this solution there were dissolved, in order, 46.6 g. (0.4 mole) allyl ether, 2.0 g. mercuric acetate, and 1.0 g. of a 45% solution of boron trifluoride in ether. The solution was heated under reflux, and the condensate led through a continuous water separator. After 3 hr., 3 g. of an aqueous layer had separated and the solution had turned quite dark. An additional 2.0 g. mercuric acetate and 1.0 g. boron trifluoride solution were added and reflux continued until another 1.5 g. of an aqueous layer had separated.

In order to remove unreacted alcohol, 5 g. boric acid was next added and reflux resumed until no further water appeared. The reaction mixture was then stripped by heating to 97° under 0.35 mm. pressure, and the residue then fractionally distilled to give 110.2 g. allyl octadecyl ether, b.p. 146–152°/0.30 mm., a yield of 71% based on octadecyl alcohol.

Acknowledgment—We wish to acknowledge the technical assistance of Mr. Charles D. Stills in a portion of this work.

PHILADELPHIA, PA.

---

[11] Microanalyses by Mr. C. W. Nash and associates.

[12] E. A. Talley, A. S. Hunter, and E. Yanovsky, *J. Am. Chem. Soc.*, **73**, 3528 (1951).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

Reactions of Succinyl Dichloride with Organometallic Reagents[1]

JAMES CASON AND ELMER J. REIST

Received May 20, 1958

The reaction of diethylcadmium with succinyl dichloride gives no 3,6-octanedione but yields instead γ-ethyl-γ-caprolactone, succinic anhydride, and both pseudo and normal ethyl esters of γ-ketocaproic acid. These products are shown to be consistent with the view that succinyl dichloride is a normal open-chain structure, but γ-ketocaproyl chloride is a cyclic structure (γ-chloro-γ-caprolactone). The reaction of ethylmagnesium bromide with succinyl dichloride also yields products consistent with the above-cited structures. Although the cadmium reaction with succinyl dichloride appears of no value for practical preparative purposes, the Grignard reaction with this dichloride furnishes a useful synthesis of γ-keto acids. The mechanism of the Grignard reaction with acid chlorides in presence of ferric chloride is discussed, and it is suggested that the key step involved, which leads to high yields of ketones, is extraction of halogen from the acid chloride by ferric chloride.

In view of recent evidence[2] that succinyl dichloride exists as the normal open-chain diacid dichloride and that γ-keto acid chlorides exist at room temperature as cyclic structures (γ-chloro-γ-lactones), it is of interest to determine whether the reactions of succinyl dichloride with Grignard and cadmium reagents yield products consistent with such structures. These reagents are selected

---

[1] This investigation was supported in part by a research grant (E-86) from the National Institutes of Health, U. S. Public Health Service. A part of these data was presented at the 127th meeting of the American Chemical Society, Cincinnati, Ohio, March 30, 1955.

[2] J. Cason and E. J. Reist, *J. Org. Chem.*, **23**, 1492 (1958).