[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BAYLOR UNIVERSITY]

Hydrogenolysis by Metal Hydrides. II. Hydrogenolysis of Aryl Vinyl Ethers by Lithium Aluminum Hydride[1]

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Aryl vinyl ethers have been hydrogenolyzed in good yields by lithium aluminum hydride to give phenols and hydrocarbons. The extent of hydrogenolysis, which was catalyzed by nickel (II) chloride and by Raney nickel, was significantly influenced by temperature and the solvent. Phenyl vinyl ether was cleaved more than 90% on treatment with excess lithium aluminum hydride and nickel chloride at 0° in bis(2-ethoxyethyl) ether, contrasted to 40% hydrogenolysis at 35° in ethyl ether. Substituents on the aromatic ring and on the vinyl group, in general, caused a decrease in the hydrogenolysis compared with phenyl vinyl ether.

INTRODUCTION

The ether linkage is generally considered stable in the presence of lithium aluminum hydride since ethers are the usual solvents for this reagent. Certain types of ethers, however, undergo hydrogenolysis readily with lithium aluminum hydride; for example, epoxides,[3] allyl aryl ethers,[4,5] and β-alkoxy- and β-aryloxypropionitriles[6] are cleaved in good yields under mild conditions. It is the purpose of this paper to report an investigation of the lithium aluminum hydride hydrogenolysis of aryl vinyl ethers.

This hydrogenolysis, which apparently has not been previously observed, has been applied to a series of nine aryl vinyl ethers by treating the ethers with a large excess of lithium aluminum hydride in a suitable solvent at reflux temperature or below and in the presence of nickel chloride. The alkyl-oxygen bond was preferentially cleaved to yield phenols and alkyl hydrocarbons. As in the various solvents the reaction was nearly complete in three hours or less, this time was arbitrarily chosen for comparative runs evaluating other variables. The extent of hydrogenolysis was measured by quantitative determination of the resultant phenol, and in general, the results were reproducible within ±3%.

The aryl vinyl ethers with the exception of β-chlorovinyl phenyl ether were obtained by dehydrohalogenation of the corresponding aryl β-haloethyl ethers, which in turn were generally prepared by the Williamson reaction. All were extensively purified to remove phenolic impurities. Several of the ethers were characterized completely with physical properties, ultraviolet spectra, and analysis for the first time.

DISCUSSION

Data presented in Table I show the effect of a variety of experimental conditions on the hydrogenolysis.

TABLE I

EFFECT OF REACTION CONDITIONS ON HYDROGENOLYSIS OF PHENYL VINYL ETHER

Solvent	Catalyst	Temp.	Time, hr.	Cleavage, %
Carb.[a]	$NiCl_2$	0°	3	93
Carb.	$NiCl_2$	35	3	61
Carb.	$NiCl_2$	35	24	61
Carb.	$NiCl_2$	65	3	52
Carb.	$NiCl_2$	100	3	47
Carb.	Raney Ni	0	3	97
Carb.	Raney Ni	35	3	80
Carb.	Black pwd.	0	3	62
THF[b]	$NiCl_2$	0	3	89
THF	$NiCl_2$	35	24	40
THF	Raney Ni	0	3	88
Dioxane	$NiCl_2$	35	3	77
Dioxane	$NiCl_2$	35	24	96
Dioxane	$NiCl_2$	65	3	61
Dioxane	$NiCl_2$	101	24	60
Ethyl ether	$NiCl_2$	35	24	38
THP[c]	$NiCl_2$	0	3	38
THP	$NiCl_2$	35	3	24
THP	$NiCl_2$	85	24	15

[a] Bis(2-ethoxyethyl) ether. [b] Tetrahydrofuran. [c] Tetrahydropyran.

The hydrogenolysis reaction was favored by low temperatures, all other variables being held constant. Using phenyl vinyl ether in bis(2-ethoxyethyl) ether at 0°, 35°, 65°, and 100°, the observed cleavages were 93%, 61%, 52%, and 47%, respectively. In dioxane the cleavage of phenyl ether was 96% at 35° but only 60% at reflux temperature. Similar results were obtained with tetrahydrofuran and tetrahydropyran as solvents. This unusual temperature effect suggests that the reaction is dependent on the formation of an intermediate complex which is stabilized at low tempera-

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[2] (a) From the thesis submitted by B.G.B. in partial fulfillment of the requirements for the M.S. degree, Baylor University, 1956. (b) Baroid Division, National Lead Co., Houston, Tex.

[3] L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 1675 (1949).

[4] P. Karrer and O. Ruttner, *Helv. Chem. Acta*, **33**, 812 (1950).

[5] Paper I in this series. V. L. Tweedie and M. Cuscurida, *J. Am. Chem. Soc.*, **79**, 5463 (1957).

[6] L. M. Soffer and E. W. Parrotta, *J. Am. Chem. Soc.*, **76**, 3580 (1954).

tures and which is broken down into reaction products upon addition of water.

Nickel (II) chloride was used as a catalyst on the basis of its use in the hydrogenolysis of the allyl aryl ethers.[5] Lithium aluminum hydride effected 13% hydrogenolysis of phenyl vinyl ether in the absence of catalyst compared with 67% in the catalyzed reaction. The effective minimum amount of catalyst was about fifteen millimoles per mole of reactant ether; however, excessive amounts were undesirable and reduced the cleavage yield. In all cases the amount of catalyst was in excess of its solubility in the solvent.

The black color which characterized the catalyzed reactions suggested that the nickel chloride was reduced by the lithium aluminum hydride. When nickel chloride was added to a solution of lithium aluminum hydride in bis(2-ethoxyethyl) ether, an energetic reaction occurred and produced a finely divided black solid resembling Raney nickel. Similar reactions were observed using tetrahydrofuran, tetrahydropyran, and ethyl ether as solvents; however, the reaction was very slow in dioxane and required heating. In all the solvents except ethyl ether the suspended black material was only partially collected by centrifugation. Dilution of these solvents with ether caused coalescence and precipitation. After decantation of the solvents and repeated washing of the precipitate with ether to remove unchanged lithium aluminum hydride, the black material reacted vigorously with water, liberating a gas which was presumed to be hydrogen. Upon exposure to air the dried solid became hot and occasionally flamed. The solid was not identified but on the basis of x-ray analysis appeared to be a nickel hydride or more probably an active form of metallic nickel, with a large amount of adsorbed hydrogen.[7,8] Many metal halides are reported to be reduced by lithium aluminum hydride to the metal hydride or in some cases to the metal.[9] The preparation of a nickel hydride or nickel by this method apparently has not been reported.

The black solid when kept under organic solvents to avoid contact with moisture and air was as effective as nickel chloride in the catalysis of the hydrogenolysis. Because of the resemblance of the solid to Raney nickel, it seemed likely that Raney nickel would also catalyze the hydrogenolysis. Indeed, Raney nickel was as effective as nickel chloride.

The solvent had a marked effect on the extent of hydrogenolysis, all other conditions being constant. The decreasing order of effectiveness of solvents for the hydrogenolysis of phenyl vinyl ether at 35° was: dioxane > bis(2-ethoxyethyl) ether > tetrahydrofuran > ethyl ether > tetrahydropyran. This order is similar to the order of solvents for the hydrogenolysis of allyl phenyl ether,[5] except that the positions of tetrahydrofuran and dioxane are exchanged. Other workers[6,10] have observed varying solvent effects in lithium aluminum hydride reactions; however, the order of effectiveness of solvents appears to be characteristic for each reaction. Wiberg[11] has shown that highly ether soluble coordination compounds are formed between nucleophilic solvents and lithium aluminum hydride, and that the number of dentates increases as the temperature decreases. Thus the observed solvent effect might be interpreted in terms of the competition between the solvent and the aryl vinyl ether for coordination with the hydride.

A series of chloro- and methyl- substituted aryl vinyl ethers was subjected to hydrogenolysis as a means of determining the effect of ring-activating and ring-deactivating groups. The conditions used for these comparative runs were those which gave moderate cleavage of phenyl vinyl ether so that any increase or decrease in cleavage caused by the substituent could be detected. The data are presented in Table II. In a similar study with allyl aryl ethers[5] it was shown that hydrogenolysis was decreased by methyl- and increased by chloro-substituents on the ring compared with the unsubstituted ether. In the aryl vinyl ethers the effect of ring substituents was not clearly defined and appeared to be highly solvent-dependent. In dioxane all of the substituted ethers, especially chloro, were cleaved less than phenyl vinyl ether. In bis-(2-ethoxyethyl) ether the chloro- and methyl-substituted compounds, with exception of the trichloro- and the trimethyl-, showed equal or greater cleavage than phenyl vinyl ether. The very sharp decrease in hydrogenolysis for both the mesityl vinyl and the 2,4,6-trichlorophenyl vinyl ethers suggests that steric factors are equally or more important than the kind of substituent on the ring.

Unsaturation in the alkyl moiety near the ether linkage has been shown an essential structural feature for significant hydrogenolysis by catalyzed lithium aluminum hydride. Negligible cleavage has been reported with phenyl propyl ether, 3-butenyl phenyl ether, β-chlorophenetole, and anisole at 65° in tetrahydrofuran[5]; phenetole and β-ethoxyphenetole were not cleaved in refluxing butyl ether.[12] Likewise, when the vinyl unsaturation was

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(7) H. K. Emeleus and J. S. Anderson, *Modern Aspects of Inorganic Chemistry*, D. Van Nostrand Co., Inc., New York, N.Y., 1952, p. 295.

(8) D. T. Hurd, *An Introduction to the Chemistry of the Hydrides*, John Wiley and Sons, Inc., New York, N.Y., 1952. p. 189.

(9) *Lithium Aluminum Hydride, General Catalog of Technical Bulletins*, Metal Hydrides, Inc., Beverly, Mass., 1955, p. 1.

(10) N. L. Paddock, *Nature*, **167**, 1070 (1951).

(11) E. Wiberg, H. Nöth, and R. Uson, *Z. Naturforsch.* **11b**, 487 (1956).

(12) Sheila Fling, M. S. thesis, Baylor University, 1958.

TABLE II

EFFECT OF STRUCTURE ON HYDROGENOLYSIS OF ARYL VINYL ETHERS[a]

Ether	Per Cent Hydrogenolysis In dioxane	Per Cent Hydrogenolysis In carb.
Phenyl vinyl	77	67
p-Tolyl vinyl	55	89
o-Tolyl vinyl	60	69
p-Chlorophenyl vinyl	53	65
o-Chlorophenyl vinyl	31	80
Mesityl vinyl	29	28
2,4,6-Trichlorophenyl vinyl	12[b]	37
β-Chlorovinyl phenyl	41[c]	42
Phenyl	5	4

[a] Reaction time, 3 hr.; temperature, 35°; catalyst, nickel (II) chloride; lithium aluminum hydride, 100% mole excess. [b] Recovered 85% of 2,4,6-trichlorophenyl vinyl ether. [c] Hydrogenolysis of chlorine was 43.2% (Volhard).

made a part of an aromatic ring—as in phenyl ether—hydrogenolysis was negligible.

Substitution of chlorine in the vinyl group greatly reduced the hydrogenolysis. It is interesting that with β-chlorovinyl phenyl ether the carbon-halogen bond underwent hydrogenolysis to the same extent as the ether linkage. It is very unlikely that after the hydrogenolysis of the ether the halogen would be quantitatively cleaved from the resulting vinyl chloride or ethyl chloride; equally unlikely would be the removal of the chlorine from the chlorovinyl ether followed by the quantitative cleavage of the resulting phenyl vinyl ether. Thus, it is proposed that the carbon chlorine and the carbon oxygen hydrogenolyses occur simultaneously or in sequence in the transition complex. The final products of the reaction must be held as complexes until decomposition with water, as no gaseous products were liberated during the reaction.

To account for the observed effects of the solvent, the catalyst, temperature, the initially rapid reaction, and the reaction products, it is proposed that the aryl vinyl ethers form reversibly intermediate complexes with the solvent and/or the hydride which then undergo hydrogenolysis by excess hydride to yield product complexes from which the final products are liberated upon decomposition with water. The reversible first step would be favored by low temperatures and by certain solvents. The catalyst may stabilize the intermediate or may catalyze its hydrogenolysis by the excess hydride.

EXPERIMENTAL

Materials. The aryl β-haloethyl ethers, which were starting materials for the preparation of the aryl vinyl ethers, were either purchased or prepared by recognized methods. The β-chlorophenetole and phenyl ether (Eastman, white label) were used without further purification. β-Bromoethyl 2,4,6-trichlorophenyl ether and β-bromoethyl mesityl ether were prepared by the method of Peak and Watkins.[13] According to the method of Clemo and Perkin,[14] *o*- and *p*-cresol were treated in basic aqueous solution with β-chloroethyl *p*-toluenesulfonate to obtain the β-chloroethyl *o*- and *p*-tolyl ethers in yields above 50%. The β-bromoethyl *o*- and *p*-chlorophenyl ethers were prepared from the corresponding chlorophenols and ethylene bromide by the Williamson reaction.[15] The observed physical constants of these several ethers were in agreement with those reported in the literature.

The anhydrous nickel (II) chloride was prepared from the hexahydrate (Baker and Adamson, reagent grade) by heating at 125° for several hours. The solvents—ethyl ether, dioxane, tetrahydrofuran, tetrahydropyran, and bis(2-ethoxyethyl) ether—were purified by drying over sodium wire, filtering, and finally distilling from lithium aluminum hydride (Metal Hydrides, Inc., Beverly, Mass.).

Dehydrohalogenation. The β-chlorophenetole and the β-bromoethyl mesityl ether were dehydrohalogenated by heating slowly 0.32 mole of the haloether with 70 g. of powdered potassium hydroxide in a 500-ml. flask arranged for simple distillation of the aryl vinyl ether as it was formed. The crude product was dried in ether solution over anhydrous sodium sulfate and purified by fractionation. Phenyl vinyl ether: yield 35%; b.p. 155–157°, reported[16] 155–156°; ultraviolet spectrum λ_{max} 270 and 225 mμ, ϵ 1,113 and 14,480, respectively. Mesityl vinyl ether: yield 50%; b.p. 200–202°; d^{25} 0.9728, d^{30} 0.9686; n_D^{25} 1.5089, n_D^{30} 1.5072; ultraviolet spectrum λ_{max} 276 mμ, ϵ 312.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.30; H, 8.80. Found: C, 81.12; H, 8.90.

To a cooled solution of 80 g. potassium hydroxide in 50 g. of 2-ethoxyethanol was added 25 g. of aryl β-haloethyl ether. Upon heating dehydrohalogenation proceeded smoothly, and the aryl vinyl ether distilled. This procedure was used to dehydrohalogenate the β-chloroethyl *o*- and *p*-tolyl ethers and the β-bromoethyl *o*- and *p*-chlorophenyl ethers to the corresponding aryl vinyl ethers. *o*-Tolyl vinyl ether: yield 76%; b.p. 167–169°, reported[16] 167–168.5°; d^{25} 0.9531, d^{30} 0.9484; n_D^{25} 1.5072, n_D^{30} 1.5050; ultraviolet spectrum λ_{max} 276, 270.5, and 225.5 mμ, ϵ 769, 923 and 8,070, respectively. *p*-Tolyl vinyl ether: yield 50%; b.p. 177–178° reported,[17] b.p. 177–178°; d^{25} 0.9509, d^{30} 0.9461; n_D^{25} 1.5077, n_D^{30} 1.5057; ultraviolet spectrum λ_{max} 275 and 228 mμ, ϵ 1,290 and 13,720, respectively. *p*-Chlorophenyl vinyl ether: yield 36%; b.p. 198–202°, reported[18] 90° (20 mm.); d^{25} 1.1118, d^{30} 1.1130; n_D^{25} 1.5356, n_D^{30}1. 5330; ultraviolet spectrum λ_{max} 279 and 232 mμ, ϵ 1170 and 18,800, respectively. *o*-Chlorophenyl vinyl ether: yield 47%; b.p. 195–198°, reported[19] b.p. 192–195°; d^{25} 1.1300, d^{30} 1.1248; n_D^{25} 1.5336, n_D^{30} 1.5310; ultraviolet spectrum λ_{max} 280, 273.5 and 226 mμ, ϵ 1245, 1184, and 8780, respectively.

Anal. Calcd. for C_8H_7OCl: C, 59.00; H, 4.54. Found: C, 59.12; H, 4.40.

For dehydrohalogenation of β-bromoethyl 2,4,6-trichlorophenyl ether, 50 g. (0.116 mole) was dissolved in an alcoholic solution of sodium ethoxide (10 g. of sodium in 150 ml. of absolute ethanol) and warmed for 40 min. The cooled reaction mixture was diluted with four volumes of water and acidified with sulfuric acid. The red oil which separated was taken up in ethyl ether, washed with water, dried over anhydrous sodium sulfate, and distilled. The yield was 42% of

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[15] C. S. Marvel and A. L. Tanenbaum, *Org. Syntheses*, **Coll. Vol. I**, 435 (1951).

[16] M. F. Shostakovskii and M. S. Burnistrova, *J. Appl. Chem.* (*U.S.S.R.*), **15**, 260 (1942).

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[18] J. M. Wilkinson, Jr., and E. S. Miller, U.S. Patent **2,695,920** (1954).

[19] M. Julia and G. Tchernoff, *Bull. soc. chim. France*, 181 (1956).

2,4,6-trichlorophenyl vinyl ether, b.p. 230–235°, reported[19] b.p. 135–40° (21 mm.); d^{25} 1.350, d^{30}1.339; n_{D}^{25} 1.5494, n_{D}^{30} 1.5474; ultraviolet spectrum $\lambda_{\max}$ 288 and 279.5 mμ, ε 652 and 627, respectively.

Anal. Calcd. for $C_8H_5OCl_3$: C, 43.00; H, 2.25. Found: C, 43.17; H, 2.41.

β-Chlorovinyl phenyl ether. To 350 ml. of absolute methanol was added 120 g. (0.9 mole) of powdered potassium phenoxide[20] and 110 g. (1.13 moles) of 1,2-dichloroethene. The solution was heated in an autoclave so that a temperature of 110° was reached in 6 hrs. and maintained for an additional 12 hrs. When cooled to room temperature, the reaction mixture was removed and steam distilled. Upon diluting the alcoholic distillate with water, the crude β-chlorovinyl phenyl ether separated as an oil and was taken up in ethyl ether for washing with 20% potassium hydroxide solution and finally with water. After drying over anhydrous calcium sulfate, the drying agent and excess ethyl ether were removed. Vacuum distillation gave 28 g. (0.18 mole) of β-chlorovinyl phenyl ether, b.p. 74–75° (5 mm.); d^{25} 1.147, d^{30} 1.141; n_{D}^{25} 1.5444, n_{D}^{30} 1.5420; ultraviolet spectrum $\lambda_{\max}$ 268 and 226 mμ, ε 1,062 and 13,560, resp.

Anal. Calcd. for C_8H_7OCl: C, 59.00; H, 4.54. Found: C, 59.16; H, 4.42.

Procedure for ether hydrogenolysis. For a typical hydrogenolysis run 100 ml. of solvent, 43–76 mg. ($3.3\text{–}5.8 \times 10^{-4}$ moles) anhydrous nickel (II) chloride, and 3 g. (0.08 mole) of finely divided lithium aluminum hydride were mixed in a 250-ml. three necked flask equipped with a dropping funnel and a reflux condenser with drying tube protection. A weighed quantity (usually about 0.03 mole) of the phenol-free aryl vinyl ether in a small amount of solvent was added. The mixture was refluxed 3 hrs., after which time it was cooled below room temperature, and the excess lithium aluminum hydride was destroyed by the slow addition of 30 ml. of water. The inorganic solids were dissolved by addition of hydrochloric acid (18%), and the organic constituents were extracted with ether to a negative Folin[21] test on the aqueous layer. The phenolic content of the ether extract was determined quantitatively by the methods used by Tweedie and Cuscurida. For reactions run at temperatures lower than the reflux temperature of the solvent, a constant temperature bath was used and the reaction mixture was agitated.

In the hydrogenolysis of β-chlorovinyl phenyl ether the reaction mixture was acidified with sulfuric acid instead of hydrochloric, and the extracted aqueous residue was analyzed for chloride by the Volhard Method.[22] A chloride blank on a reaction mixture without β-chlorovinyl phenyl ether present was used to correct for the nickel chloride catalyst and the trace of chloride in the lithium aluminum hydride.

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