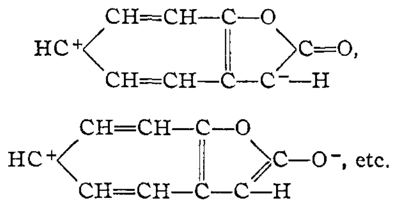
If the monohydrate complex persists in the solution with the moments of its component parts directed in parallel, its moment is calculated as 2.60 + 1.75 = 4.35 D. in good agreement with the observed value, 4.39 D. In this connection, it is desirable that X-ray crystal analysis be carried out on the monohydrate.

The large increase, about 1.52 D., in moment of 1-oxaazulan-2-one, 5.64 D., over those of γ-lactones represented by that of γ-butylolactone,[20] 4.12 D., seems to indicate the contribution to resonance of polar structures such as



An analogous case already has been reported by Di Giacomo and Smyth,[21] who found a large increase, about 1.4 D., in the moment of cycloheptatrienone over those of other cyclic ketones. On the other hand, the increase in moment of 1 azaazulan-2-one, 2.73 D., over that of 2-pyrrolidone, 2.3 D.,[22] is not so great as that predicted by the same reasoning. This suggests the following explanation in terms of hydrogen bonding. Unlike 1-oxaazulan-2-one, 1-azaazulan-2-one has an NH group capable of forming a hydrogen bond with the oxygen atom of another molecule. The formation of dimers having an almost vanishing moment in dilute solutions would lead to the decrease of observed moment of 1-azaazulan-2-one below the true moment of a single molecule of this compound.

Acknowledgment.—We wish to express our cordial thanks to Prof. Nozoe and his collaborators for providing us with the purified materials used in the present investigation.

(20) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936).

(21) A. Di Giacomo and C. P. Smyth, THIS JOURNAL, **74**, 4411 (1952).

(22) G. Devoto, *Gazz. chim. ital.*, **63**, 495 (1933); *cf.* E. Fischer, *J. Chem. Soc.*, 4525 (1952).

CHIKUSA, NAGOYA, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BAYLOR UNIVERSITY]

Hydrogenolysis by Metal Hydrides. I. Hydrogenolysis of Aryl Allyl Ethers by Lithium Aluminum Hydride[1]

BY VIRGIL L. TWEEDIE AND MICHAEL CUSCURIDA[2]

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Lithium aluminum hydride has been found to be an effective hydrogenolytic agent for aryl allyl ethers, the reaction products being phenols and alkenes. The hydrogenolyses were catalyzed by a number of salts and metallic oxides of which nickel(II) chloride was most frequently used. The extent of cleavage was markedly influenced by the nature of the solvent and by the type of substituent groups on the aryl ring and the allylic chain. Hydrogenolysis of phenyl allyl ether at 35° was 86% in tetrahydrofuran, 18% in ethyl ether and 59% in dioxane. Chloro groups in the *ortho* and *para* positions and phenyl and chloro groups on carbon three of the allylic system generally enhanced the hydrogenolysis reaction; methyl groups in the corresponding positions decreased the extent of cleavage compared to that of phenyl allyl ether. Phenyl *n*-propyl ether and phenyl 3-butenyl ether were not cleaved under the conditions employed.

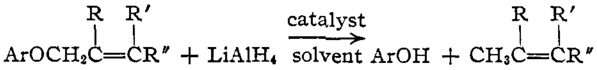
Introduction

Although the hydrogenolysis of various types of organic compounds by complex metal hydrides has been reported frequently, there are relatively few reports of the hydrogenolysis of ethers by lithium aluminum hydride. Karrer and Ruttner[3] reported 26% cleavage of phenyl allyl ether and 10% cleavage of phenyl benzyl ether, using ethyl ether as a solvent and cobalt(II) chloride as a catalyst. Soffer and Parrotta[4] found that in the lithium aluminum hydride reduction of β-alkoxy- and β-aryloxypropionitriles to the corresponding amines, there was considerable cleavage of the alkoxy and aryloxy groups to give *n*-propylamine and alcohols or phenols. Other compounds containing ether linkages which undergo hydrogenolysis by lithium aluminum hydride are epoxides,[5] solasodine[6] and sapogenins.[7]

It was the purpose of this investigation to determine the general applicability of lithium aluminum hydride as a hydrogenolytic agent for aryl allyl ethers and to study the influence of catalysts, reaction conditions and molecular structure.

Discussion

The work of Karrer and Ruttner was verified although with somewhat lower yields. Fourteen aryl allyl ethers have been cleaved in good yields by reaction in a solvent for 24 hr. with a catalyst and an excess of lithium aluminum hydride. All underwent hydrogenolysis at the alkyl oxygen bond to form a phenol and an alkene.



$$\mathrm{ArOCH_2}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}{=}\overset{\mathrm{R'}}{\overset{|}{\mathrm{C}}}\mathrm{R''} + \mathrm{LiAlH_4} \xrightarrow[\text{solvent}]{\text{catalyst}} \mathrm{ArOH} + \mathrm{CH_3}\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}{=}\overset{\mathrm{R'}}{\overset{|}{\mathrm{C}}}\mathrm{R''}$$

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(1) Paper presented at March, 1954, A.C.S. Meeting, Kansas City, Mo.

(2) From the dissertation submitted by Michael Cuscurida in partial fulfillment of the requirements for the Ph.D. degree, Baylor University, 1955.

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

(4) L. M. Soffer and E. W. Parrotta, THIS JOURNAL, **76**, 3580 (1954).

(5) L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

(6) L. H. Briggs and R. H. Locker, *J. Chem. Soc.*, 3020 (1950).

(7) H. M. Doukas and T. D. Fontaine, THIS JOURNAL, **73**, 5917 (1951).

In no case was aryl oxygen fission observed. The extent of cleavage was measured by quantitative determination of phenols. Hydrogenolysis runs were made in duplicate; in general, results were reproducible within ±3%.

The ethers used in this work were prepared by various modifications of the Williamson reaction.[8,9] All were purified extensively to remove completely phenolic impurities. Two ethers, mesityl allyl and phenyl β-phenylallyl, which have not previously been reported were prepared and characterized.

Catalysis of the Ether Hydrogenolysis Reaction.—The data from runs designed to study catalytic effects are given in Table I. Several runs were made with each catalyst and the data presented are typical.

TABLE I

SALTS CATALYZING THE LITHIUM ALUMINUM HYDRIDE CLEAVAGE OF PHENYL ALLYL ETHER

Reaction time, 24 hr., solvent, tetrahydrofuran, 65°

Catalyst	Catalyst concn., moles × 10^{-3} per mole ether	Cleavage, %
$NiCl_2$	41.6	0.0[a]
None		12.4[b]
$NiCl_2$	41.6	82.6
$CoCl_2$	62.4	44.0
$MnCl_2$	64.5	46.0
CuCl	81.9	57.6
$CuCl_2$	40.2	60.0
$SnCl_2$	14.3	17.1
Hg_2Cl_2	5.9	12.7
$FeCl_2 \cdot 4H_2O$	42.7	19.7
$FeCl_3$	16.6	22.4
KCl	72.5	13.7
Cu_2O	37.8	10.3
CuO	68.0	44.8
$Cu(C_2H_3O_2)_2$	29.8	29.9
$CuSO_4$	34.5	8.5
$NiSO_4$	35.0	18.4
$Ni(NO_3)_2 \cdot 6H_2O$	29.6	86.6
$AlCl_3$	40.4	38.1

[a] Catalyst only, no lithium aluminum hydride. [b] Lithium aluminum hydride only, no catalyst.

In no case did the salts used as catalysts cause ether cleavage in the absence of lithium aluminum hydride. On the other hand, lithium aluminum hydride alone caused 12% hydrogenolysis of phenyl allyl ether after 24 hr. in boiling tetrahydrofuran. The catalytic effect of certain inorganic salts, particularly the chlorides of nickel(II), cobalt(II), manganese(II), copper(I) and (II) is illustrated by the high cleavage yields obtained with phenyl allyl ether. Certain other salts, the chlorides of tin(II), mercury(I), iron(II) and (III), potassium and others exhibited little or no catalytic effect on the ether hydrogenolysis.

It should be noted that the amount of catalyst used was in excess of its solubility in tetrahydrofuran. While these salts varied considerably in their solubility, there appeared to be no correlation between catalytic activity and solubility. The data for copper(II) and copper(I) oxide are of interest in that the highly insoluble ionic copper(II) oxide showed much more catalytic activity than the more soluble, covalent copper(I) oxide.

The nature of the anion, as well as the cation, appears to play an important role in the catalytic activity of the salt. In a series of runs made with various copper(II) salts the catalysis decreased markedly as the anion component was varied in the order—chloride, acetate, sulfate. A similar study with nickel salts showed that the chloride and nitrate possessed about the same catalytic activity and were far superior to the sulfate. Nickel(II) chloride was used at a fixed concentration as the catalyst when other variables were investigated.

Effects of Solvent and Temperature on Ether Cleavage.—Soffer and Parrotta[4] found that the β-alkoxy- and β-aryloxypropionitriles were cleaved by lithium aluminum hydride to a much greater extent in tetrahydrofuran than in ethyl ether even when the reaction was carried out at the temperature of boiling ethyl ether. Since in preliminary runs we also had observed a solvent effect, a series of experiments was designed to find the influence of various solvents. The results are presented in Table II. The nature of the solvent rather than the reaction temperature appeared to be an important factor in determining the extent of cleavage in a 24 hr. run. For example, when five different solvents were used at 35°, the cleavage of phenyl allyl ether decreased from 86% in tetrahydrofuran to 18% in ethyl ether. While phenyl allyl ether was cleaved significantly less in isopropyl ether than in tetrahydrofuran, in a given solvent the cleavage was essentially the same at 35° and at reflux temperature. As further evidence of the "catalytic" influence of the solvent two runs using ethyl ether and tetrahydrofuran mixtures of varying concentrations showed that as little as 10% tetrahydrofuran in ethyl ether nearly doubled the amount of cleavage.

TABLE II

EFFECT OF SOLVENT ON CLEAVAGE OF PHENYL ALLYL ETHER

Reaction time, 21–24 hr.; catalyst, 41.6 × 10^{-3} mole $NiCl_2$ per mole of ether

Solvent[a]	Temp., °C.	Cleavage, %
Et_2O	35	18.1
THF	65	86.2
THF	35	89.4
10% THF–90% Et_2O	35	32.3
30% THF–70% Et_2O	35	53.2
i-Pr_2O	69	49.5
i-Pr_2O	35	56.8
Dioxane	101	84.7
Dioxane	35	59.2
Dioxane	101	4.3[b]
Carb.	35	74.5

[a] Abbreviation for solvents: THF, tetrahydrofuran; Et_2O, ethyl ether; i-Pr_2O, isopropyl ether; carb., diethyl carbitol. [b] Solvent only, no lithium aluminum hydride nor catalyst.

It was not possible to use diethyl carbitol at its boiling point since at this temperature the aryl allyl ethers undergo the Claisen rearrangement. Phenyl allyl ether was moderately stable below 100° since in dioxane after 24 hr. under reflux only

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(8) L. Claisen, *Ann.*, **418**, 69 (1919).

(9) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 296.

4.3% was cleaved or converted to phenolic substances.

Tetrahydrofuran was considered the best solvent for the reaction and was used in runs when other reaction variables were studied.

Effect of Time.—Several runs were made with phenyl benzyl ether in tetrahydrofuran at 65° in which only the reaction time was varied. It appeared that the cleavage was substantially complete at the end of 12 hr. However, since the effect of time was not determined for the other ethers, which may react at somewhat different rates, most cleavage runs were for 24 hr. periods.

Effect of Substitution on the Aryl Ring and the Allylic Chain.—As a means of determining the general applicability of the hydrogenolysis reaction and as a means of studying the influence of substituents, a number of aryl allyl ethers substituted either on the aryl ring or the allylic chain were prepared and subjected to hydrogenolysis. Data from typical runs are given in Table III.

TABLE III

EFFECT OF STRUCTURE ON ETHER CLEAVAGE

Reaction time, 24 hr.; catalyst, 0.2 g. $NiCl_2$/50 ml. solvent; $LiAlH_4$, 100% mole excess

Ether	Temp., °C.	Cleavage, % in THF	In Et_2O
A. Ring substitution			
Phenyl allyl	35	89.4	18.1
Phenyl allyl	65	86.2	
o-Tolyl allyl	35	71.9	18.3
o-Tolyl allyl	65	73.1	
Mesityl allyl	35	62.1	7.8
Mesityl allyl	65	58.5	
o-Chlorophenyl allyl	35		44.5
o-Chlorophenyl allyl	65	87.0	
2,4,6-Trichlorophenyl allyl	35	46.4	46.9
2,4,6-Trichlorophenyl allyl	65	72.1	
1-Naphthyl allyl	65	76.1	
B. Allylic chain substitution			
Phenyl crotyl	35	22.0	6.8
Phenyl crotyl	65	38.7	
Phenyl methallyl	35	39.7	5.6
Phenyl methallyl	65	34.3	
Phenyl γ-chloroallyl	65	87.0	
Phenyl 3-chloro-2-butenyl	35	22.5	4.3
Phenyl 3-chloro-2-butenyl	65	20.5	
Phenyl cinnamyl	35	91.0	
Phenyl cinnamyl	65	97.0	
Phenyl β-phenylallyl	65	0.0	
Phenyl benzyl[a]	35		6.4
Phenyl benzyl[a]	65	19.1	
C. Other			
Phenyl *n*-propyl	65	3.8	
Phenyl *n*-propyl	190 (in carb.)	9.0	
Phenyl 3-butenyl	65	5.0	
2-Naphthyl benzyl	65	65.0	
1-Naphthyl benzyl	35	55.4	
1-Naphthyl benzyl	65	88.0	

[a] The catalyst was $CoCl_2$ instead of $NiCl_2$.

Assuming that the electron density of the oxygen atom is an important factor in the hydrogenolysis reaction, it was expected that substitution of ring-activating or ring-deactivating groups in the *ortho* and *para* positions would have a significant effect on the extent of ether cleavage. The methyl and chloro groups were selected as substituents in most cases, since their steric requirements[10] are approximately the same and neither is attacked by lithium aluminum hydride.

The presence of the ring-activating methyl group on the benzene ring caused a decrease in the amount of cleavage compared with phenyl allyl ether. While the cleavages of *o*-tolyl allyl ether and phenyl allyl ether were the same in ethyl ether, there was slightly less cleavage of the methyl-substituted compound in tetrahydrofuran. The influence of the methyl group is shown clearly by comparison of the data for mesityl allyl ether and phenyl allyl ether.

The results of runs with *o*-chlorophenyl allyl and 2,4,6-trichlorophenyl allyl ethers indicated that substitution of the deactivating chloro group significantly enhanced hydrogenolysis in ethyl ether when compared with phenyl allyl ether and the corresponding methyl-substituted ether. In tetrahydrofuran, the chloro substituent appeared to have little or no effect. However, in every case except one the chloro-substituted ether was cleaved to a greater extent than the corresponding methyl-substituted ether. It is probable that the steric influences in the tri-substituted ethers become important relative to the electronic effects and, therefore, comparisons with phenyl allyl ether are invalid. Since in the mesityl allyl ether the steric and electronic effects would be complementary while in the trichlorophenyl allyl they would tend to cancel, the data are consistent with what would have been predicted.

The nature and location of substituents on the allylic chain was found also to have a marked effect on the extent of hydrogenolysis. Those ethers with a chloro or a phenyl group in the γ-position, such as phenyl γ-chloroallyl and phenyl cinnamyl ether, were cleaved somewhat more than phenyl allyl ether. In contrast with the 91% cleavage obtained with phenyl cinnamyl ether, the isomeric phenyl β-phenylallyl ether was not cleaved at all. Since, unfortunately, the corresponding β-chloro compound was not available, the consequence of moving the chloro group from the γ- to the β-position was not determined.

On the other hand, phenyl methallyl and phenyl crotyl ether with the methyl group in the β- and γ-positions, respectively, were cleaved much less than phenyl allyl ether. Furthermore, replacement of both hydrogens in the γ-position by methyl and chloro groups as in phenyl 3-chloro-2-butenyl ether decreased the cleavage from 89 to 22%.

It is interesting that the hydrocarbon isolated from phenyl cinnamyl ether was not the expected propenylbenzene but was found to be chiefly allylbenzene. Thus, it appears that a shift in the double bond occurred during hydrogenolysis of this ether. Whether or not an allylic shift occurs in all cases and is a part of the mechanism of the reaction has not yet been determined.

The solvent effect which was noticed with phenyl allyl ether was found also with many of the other ethers, namely, *o*-tolyl allyl, mesityl allyl, phenyl methallyl, phenyl 3-chloro-2-butenyl and phenyl cinnamyl.

[10] R. Adams and H. C. Yuan, *Chem. Revs.*, **12**, 284 (1933).

That an allylic system is necessary for the ether hydrogenolysis to be significant is indicated since the phenyl *n*-propyl and phenyl 3-butenyl ethers were cleaved less than 10% even under drastic conditions. However, aryl vinyl ethers have been found susceptible to hydrogenolysis by lithium aluminum hydride and these will be the subject of a later paper.

Experimental

Materials.—The phenols, except mesitol, were reagent grade and were used without further purification. Mesitol was synthesized by the sequence: acetone → mesitylene[11a] → nitromesitylene[11b] → mesidine[12] → mesitol.[13] The alkyl and allylic halides, benzyl chloride, methallyl chloride, *n*-propyl bromide, 1,4-dibromobutane (all Eastman, yellow label), 1,3-dichloropropene (Shell) and 1,3-dichloro-2-butene (du Pont) were checked for peroxides and were fractionated prior to use. Crotyl bromide,[14] cinnamyl bromide[15] and 3-bromo-2-phenyl-1-propene[16] were synthesized. All the salts used as catalysts were Baker and Adamson reagent grade and were used in anhydrous form unless otherwise indicated. The solvents, ethyl ether (General Chemical, reagent), tetrahydrofuran, diethyl carbitol, 1,4-dioxane (all Eastman, white label) and isopropyl ether (Fisher) were purified prior to use by drying over sodium wire, filtering and finally distilling from fresh sodium wire. Lithium aluminum hydride was purchased from Metal Hydrides, Inc., Beverly, Mass.

Stock solutions of lithium aluminum hydride in ethyl ether and tetrahydrofuran were prepared in the usual manner; the "carbitol" reagent was prepared using diethyl carbitol according to the procedure of Goodman.[17]

Preparation of Aryl Allyl Ethers.—The ethers, with the exception of mesityl allyl and 1-naphthyl benzyl, were prepared according to Claisen's modification of the Williamson reaction. To one mole of the phenol salt, formed from the phenol and potassium carbonate in 800 ml. of refluxing acetone, was added dropwise a slight molar excess of the appropriate halide. After several hours under reflux the halide salt was dissolved with water and the crude ether separated. An ether solution of the crude product was washed with dilute sodium hydroxide solution until all traces of the phenol were removed as indicated by a negative Folin test.[18] The crude aryl allyl ether was finally purified by vacuum distillation or by recrystallization from a suitable solvent.

Claisen and Eisleb[19] reported that 1-naphthyl allyl ether could not be distilled even *in vacuo* without rearrangement to allyl 1-naphthol. The literature does not report physical constants for this ether. Our attempts to purify 1-naphthyl allyl ether by reduced pressure distillation or by partially freezing the crude material were without success. In an effort to gain some degree of purification of the crude ether (naphthol-free), the dark viscous oil in benzene was passed through a two-foot column of alumina which removed considerable color. Although of doubtful purity the decolorized 1-naphthyl allyl ether was used in hydrogenolyses. These physical constants were observed: n^{25}_{D} 1.6038, d^{25}_{4} 1.0657.

The 1-naphthyl benzyl ether and mesityl allyl ether were prepared by a standard procedure.[9] 1-Naphthyl benzyl ether was purified by vacuum distillation and finally by crystallization twice from ethanol. The mesityl allyl ether was vacuum distilled; b.p. 93–97° (18 mm.), n^{25}_{D} 1.5078.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.90; H, 8.94.

The observed physical constants for the several ethers were in agreement with the values reported in the literature for these compounds. These refractive indices, not previously reported, were observed: phenyl 3-butenyl ether, n^{20}_{D} 1.4930; phenyl β-phenylallyl ether, n^{20}_{D} 1.5794.

Procedure for Ether Hydrogenolysis.—The following general procedure was used for all the ether hydrogenolyses. Five grams of the aryl allyl ether was placed in a flask along with 50 ml. of solvent and the catalyst. A stock solution of lithium aluminum hydride, in the same solvent, was added dropwise at such a rate as to maintain refluxing. When the addition was complete, the reaction mixture was refluxed for 24 hr. At least a 100% mole excess of lithium aluminum hydride was used in all runs. When the reaction was at a temperature lower than that of the refluxing solvent, the mixture was stirred during the reaction period. The flask was cooled and the excess lithium aluminum hydride was decomposed with moist ether after which 50 ml. of 18% hydrochloric acid was added. The organic layer was separated and the aqueous layer extracted with ethyl ether. These were combined for identification and quantitative determination of the cleavage products.

In cases where stock solutions were impractical because of the low solubility of lithium aluminum hydride, a slurry in the solvent was kept well stirred as the aryl allyl ether was added.

Qualitative and Quantitative Determination of Phenols.—The phenols isolated from the cleavage reactions were identified by their physical constants and preparation of known derivatives.

For quantitative determination of the phenols the combined ether extracts were washed with a 5% solution of sodium hydroxide until the washings failed to give a Folin test. These were acidified and diluted to one liter from which a suitable aliquot was used for phenol determination by the procedure of Siggia.[20] With *o*- and *p*-cresol the Siggia procedure gave results which were not reproducible and were 10–25% high, possibly due to some substitution of the methyl hydrogens or other bromine consuming reactions. A modified procedure whereby the cresol solutions were brominated at 25° for 3 min. in the dark, after which the usual procedure of Siggia was followed, gave results somewhat high but reproducible within ±2%. A factor of 0.926 was used to correct the results for the cresols.

The 1-naphthol, 2-naphthol, 2,4,6-trichlorophenol and mesitol were determined by isolation and weighing the phenol.

Determination of Hydrocarbons from Ether Hydrogenolyses.—The ethyl ether solution of reaction products, after basic extraction of the phenol, was dried and the solvent removed on a steam-bath. A micro-distillation of the residue yielded the liquid hydrocarbon. Toluene was identified by boiling point and preparation of its trinitro derivative. Allylbenzene, from cleavage of phenyl cinnamyl ether, was identified by boiling point and ultraviolet absorption peaks.[21] Using a Beckman Model D.K. recording spectrophotometer, the characteristic wave lengths 2680, 2650, 2620, 2590 and 2540 Å. were observed. The probable presence of some propenylbenzene was suggested by faint maxima at 2930 and 2840 Å., which are characteristic for propenylbenzene.

If the hydrocarbon were a gas, it was condensed and collected in a series of Dry Ice-acetone cold traps. Propene was brominated and the 1,2-dibromopropane was identified by physical constants. The hydrocarbons resulting from hydrogenolysis of phenyl crotyl, phenyl methallyl, phenyl 3-chloro-2-butenyl and phenyl 2-chloroallyl ethers were not isolated nor identified because of the small quantities of materials.

WACO, TEXAS

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(11) (a) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 341; (b) Coll. Vol. II, p. 449. Higher yields and a better crystalline product of nitromesitylene were obtained by avoiding the atmospheric distillation and instead recrystallizing the crude material several times from methanol.

(12) Reduction of nitromesitylene was with tin and hydrochloric acid at 90°. Yield of mesidine was 76%; b.p. 228–230° (lit. 229–230°, A. Ladenberg, *Ann.*, **179**, 163 (1875)).

(13) C. W. Porter and F. H. Thurber, THIS JOURNAL, **43**, 1194 (1921).

(14) A. Juvala, *Ber.*, **63B**, 1989 (1930).

(15) L. Claisen and E. Tietze, *ibid.*, **58B**, 275 (1925).

(16) L. F. Hatch and T. L. Patton, THIS JOURNAL, **76**, 2705 (1954).

(17) I. Goodman, *J. Chem. Soc.*, 2209 (1951).

(18) O. Folin and V. Ciocalteu, *J. Biol. Chem.*, **73**, 629 (1927). Folin's reagent was used extensively both to detect trace quantities of phenolic compounds during the purification of ethers and to determine the presence of phenols after hydrogenolysis of ethers. The reagent has been found capable of detecting phenolic compounds in concentrations as low as 3 p.p.m. Even after a negative ferric chloride test was obtained, usually 10–15 additional extractions with base were necessary to get a negative Folin test.

(19) L. Claisen and O. Eisleb, *Ann.*, **401**, 21 (1913).

(20) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 111.

(21) T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, THIS JOURNAL, **69**, 880 (1947).