Rearrangement of Allyl Phenyl Ethers

F. M. SONNENBERG

*Contribution No. 204 from Elastomer Chemicals Department,
E. I. du Pont de Nemours and Company, Inc.,
Wilmington, Delaware 19898*

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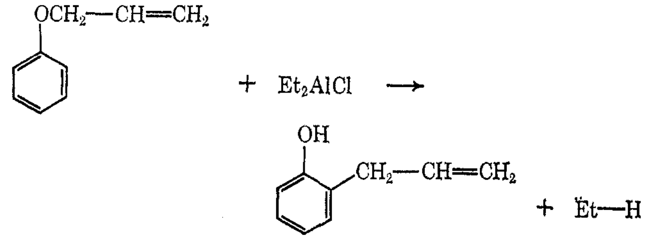
It has been found that allyl phenyl ethers undergo a facile rearrangement in the presence of alkylaluminum halides. Other workers have reported that Lewis acids such as boron trifluoride–acetic acid complex[1] or boron trichloride[2-4] cause an acid-catalyzed Claisen rearrangement. In addition when allyl phenyl ether was treated with aluminum bromide[5] in chlorobenzene, an adduct formed which was believed to have arisen from an intramolecular path in which allyl phenyl ether was first converted to *o*-allylphenol, then isomerized to the propenyl compound, which then adds to chlorobenzene.

Treatment of allyl phenyl ether in hexane with an excess of diethylaluminum chloride at room temperature resulted in the evolution of gas. Gas chromatographic analysis of the gas sample showed that at least 99% was ethane and the remainder ethylene. Decomposition of the reaction mixture with dilute acid afforded *o*-allylphenol in nearly quantitative yield. Gas chromatographic analysis of the isolated product showed that about 97% was *o*-allylphenol.



When ethylaluminum dichloride was substituted for diethylaluminum chloride, the rearrangement also occurred with the evolution of gas. However, a side product, 2-methylcoumaran, began to be formed in increasing amounts as shown in Table I. This additional product was not unexpected, as it had been reported[6] that treatment of *o*-allylphenol with acidic reagents resulted in the formation of 2-methylcoumaran. Treatment of *o*-allylphenol with the aforementioned aluminum alkyls leads to the formation of 2-methylcoumaran.

When the less acidic[7] triethylaluminum was substituted for diethylaluminum chloride, no rearrangement or gas evolution occurred. Use of triisobutylaluminum gave the same results as triethylaluminum, but use of the more acidic diisobutylaluminum chloride resulted in rearrangement without visual gas evolution.

TABLE I

REARRANGEMENT OF ALLYL PHENYL ETHER WITH ALUMINUM ALKYLS[a]

Aluminum alkyl	*o*-Allylphenol,[b] %	2-Methylcoumaran,[b] %
Diethylaluminum chloride	92.7	nil
Ethylaluminum sesquichloride	89.8	2.9
Ethylaluminum dichloride	68.1	18.2
Diisobutylaluminum chloride	95.8	nil

[a] Reaction was carried out as described in the general procedure. [b] Determined by vapor phase chromatographic analysis using a 10% polyphenyl ether (6 ft × $^1/_8$ in.) column at 140–200° programmed at 8°/min.

In contrast to the boron trichloride catalyst,[4] the aluminum alkyl can be used to rearrange allyl aryl ethers bearing electron-withdrawing groups on the aromatic ring, as shown in Table II. Consequently, a detailed study of substituted allyl chlorophenyl ethers was undertaken. Allyl *o*-, *m*- and *p*-chlorophenyl ethers were found to rearrange to allylchlorophenols in nearly quantative yields with the allyl group being *ortho to the phenolic group.*

TABLE II

REARRANGEMENT OF ALLYL PHENYL ETHERS WITH DIETHYLALUMINUM CHLORIDE[a]

Starting material	Major product	Yield, %
Allyl phenyl ether	*o*-Allylphenol	93
Allyl *o*-chlorophenyl ether	2-Allyl-6-chlorophenol	94
Allyl *m*-chlorophenyl ether	2-Allyl-5-chlorophenol	92
Allyl *p*-chlorophenyl ether	2-Allyl-4-chlorophenol	89
Allyl 2,4-dichlorophenyl ether	2-Allyl-4,6-dichlorophenol	95
Allyl 2,4,5-trichlorophenyl ether	2-Allyl-3,4,6-trichlorophenol	96
2-Alloxypyridine	Starting material	
Allyl phenyl sulfide	Starting material	

[a] Reaction was carried out as described in the general procedure.

When the preferential ortho position for rearrangement is not blocked, as with allyl 2,4,5-trichlorophenyl ether, a normal "Claisen type" rearrangement occurs to form 2-allyl-3,4,6-trichlorophenol in nearly quantitative yield at room temperature when diethylaluminum chloride is used.

When the preferential ortho positions for rearrangement are blocked, as with allyl 2,6-dichlorophenyl ether, two major reactions occur in the presence of diethylaluminum chloride. The first is the rearrangement to form 4-allyl-2,6-dichlorophenol in 43% yield and 5% 2-allyl-4,6-dichlorophenol and the second reaction is cleavage of the allyl group to form 50% 2,6-dichlorophenol. In addition, gas chromatographic analysis showed 2% unreacted starting material.

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If the preferential positions for migration of the allyl group are blocked, as with allyl 2,4,6-trichlorophenyl ether, cleavage of the allyl group is the major reaction upon treatment with diethylaluminum chloride, to form 2,4,6-trichlorophenol in 96% yield. However, substitution of benzene for hexane as the solvent causes the formation of 35% allylbenzene and 13% 1,2-diphenylpropane as well as a 94% yield of 2,4,6-trichlorophenol. Treatment of allylbenzene in benzene with diethylaluminum chloride results in formation of 1,2-diphenylpropane as the major product.

Other compounds such as 2-alloxypyridine[8] or allyl phenyl sulfide[9] which are known to undergo the thermal Claisen rearrangement failed to rearrange when treated with diethylaluminum chloride at room temperature.

Experimental Section

The nmr spectra were obtained from a Varian HA-100 spectrometer with tetramethylsilane as internal standard. The infrared spectra were taken on a Perkin-Elmer Infracord. The gas chromatograph used for analyzing the composition of the off gases was F & M Model 5750, with a 5 ft × $^1/_4$ in. column containing a 80–100 mesh Porapak S support. The same instrument was used for analyzing the composition of allyl phenyl ether reaction mixture using a 6 ft × $^1/_8$ in. column containing 10% polyphenyl ether on 80–100 mesh Gas Chrom Q support. The allyl chlorophenyl ethers were analyzed with an F & M Model 720 using a 10 ft × $^1/_4$ in. column containing 28.6% Apiezon L on a 60–80 mesh Gas Chrom Z support. The product ratios obtained by glc were derived from the peak area ratios.

The following compounds were prepared according to the procedure of Tarbell and Wilson:[10] allyl *o*-, *m*-, *p*-chlorophenyl ether; allyl 2,4-dichlorophenyl ether; allyl 2,6-dichlorophenyl ether; and allyl 2,4,5-trichlorophenyl ether. The following compounds were prepared by published procedures: allyl 2,4,6-trichlorophenyl ether;[11] 2-allyl-6-chlorophenol;[12] 2-alloxypyridine;[13] and allyl phenyl sulfide.[9] Yields and physical properties were in good agreement with literature values.

Organoaluminum compounds used in this work were purchased from Texas Alkyls. Solvents were purified and dried by conventional methods and distilled prior to use. Reactions involving the organoaluminum reagents were carried out under dry nitrogen with the usual precautions for the rigorous exclusion of moisture and air.

General Procedure.—In a typical procedure, to a solution of 0.01 mol of allyl phenyl ether in 50 ml of hexane was added 0.02 mol of diethylaluminum chloride in hexane. After stirring for 30 min, the reaction mixture was hydrolyzed below 5° with dilute hydrochloric acid. The upper layer was separated and concentrated on a rotary evaporator.

Reaction of Allyl 2,4,6-Trichlorophenyl Ether with Diethylaluminum Chloride. A. In Hexane.—To 23.7 g (0.10 mol) of allyl 2,4,6-trichlorophenyl ether in 500 ml of hexane was added 0.15 mol of diethylaluminum chloride in hexane. After stirring for 3 hr, the reaction mixture was worked up below 5° by hydrolysis with dilute hydrochloric acid. The upper layer was separated and treated with a solution of 10 g of sodium hydroxide in 300 ml of water. The aqueous phase was acidified with dilute hydrochloric acid. The solids were filtered and air dried. There was obtained 18.9 g (95.8%) of 2,4,6-trichlorophenol melting at 65-66° (lit.[11] mp 67°).

B. In Benzene.—The reaction was carried out in the same manner using 400 ml of benzene, except that in the work-up 18.5 g (93.5%) of 2,4,6-trichlorophenol was isolated from the aqueous phase. On distillation of the organic phase through a short fractionating column, there was obtained 4.1 g (34.8%) of liquid, bp 67–70° (20 mm), whose infrared spectrum was identical with that of allylbenzene, and 2.6 g (13.3%) of 1,2-diphenylpropane, bp 90–95° (0.5 mm), whose infrared spectrum was identical with that of an authentic sample, No. 2266 API Research Project 44.

Reaction of Allylbenzene with Diethylaluminum Chloride.—To a well-stirred solution of 11.9 g (0.10 mol) of allylbenzene in 300 ml of benzene was added 0.05 mol of diethylaluminum chloride in benzene. The mixture was kept at 60° for 30 min and stirred for an additional 30 min at room temperature. After hydrolysis below 10° with dilute hydrochloric acid, the upper layer was separated and concentrated on a rotary evaporator. Distillation gave 3.4 g (28.6%) of starting material, bp 60–62° (10 mm), and 3.9 g (39.8%) of 1,2-diphenylpropane, bp 121–125° (4 mm). *Anal.* Calcd for $C_{15}H_{16}$: C, 91.9; H, 8.1. Found: C, 92.0; H, 8.0. There remained behind 3.8 g of higher boiling material.

Registry No.—Allyl phenyl ether, 1746-13-0; diethylaluminum chloride, 96-10-6; ethylaluminum dichloride, 563-43-9; diisobutylaluminum chloride, 1779-25-5; allyl *o*-chlorophenyl ether, 20788-42-5; allyl-*m*-chlorophenyl ether, 24824-86-0; allyl *p*-chlorophenyl ether, 13997-70-1; allyl 2,4-dichlorophenyl ether, 5441-16-7; allyl 2,4,5-trichlorophenyl ether, 16516-83-9; 2-alloxypyridine, 5831-77-6; allyl phenyl sulfide, 5296-64-0; 1,2-diphenylpropane, 5814-85-7.

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Oxidation of Carboxylic Acids and Anhydrides to Symmetrical Esters with Higher Valency Iodine

G. BRYANT BACHMAN,[1] GEORGE F. KITE,
SAIME TUCCARBASU,[2] AND GERALD M. TULLMAN[3]

*Department of Chemistry, Purdue University,
Lafayette, Indiana 47907*

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Iodine in its higher valency forms can oxidize aliphatic acids or their anhydrides to symmetrical esters and carbon dioxide. The most efficient process involves the use of iodine triacylates and mercuric oxide and produces the corresponding esters in 70–90% yields for unbranched anhydrides. The synthesis is believed to involve a free-radical chain mechanism initiated by a homolytic thermolysis of an iodine–oxygen bond. Mercuric iodate and acid anhydrides also produce esters and, in the presence of olefins or ketones, produce olefinic or ketonic esters. Iodine triacylates are readily obtained by ozonation of solutions of iodine in aliphatic carboxylic acid anhydrides.

Recently, it was reported that tetravalent lead and iodine will oxidize carboxylic acids to symmetrical esters and carbon dioxide in substantial yields.[4] The synthesis was shown to proceed in three separate steps, only the last of which was established and was shown to be a displacement reaction between lead(II) carboxylates and alkyl iodides. The present work was undertaken in an effort to determine the natures of the first two steps in the synthesis and if possible to develop a better synthesis for symmetrical esters.

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[1] To whom correspondence should be addressed.

[2] Deceased.

[3] Commercial Solvents Corporation Research Assistant, 1966–1968.

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