[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY AND MIAMI UNIVERSITY]

# The Effect of Halogen Substituents on the Rearrangement of Allyl Aryl Ethers. I. Ethers which Rearrange Normally

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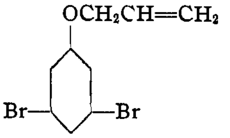
Many allyl aryl ethers have been pyrolyzed since Claisen's[1] first report on the effect of heat on these ethers. Although several types have been included in this development comparatively few halogen-substituted allyl aryl ethers have been studied. Claisen[2] and his co-workers have reported that, when heated, allyl *p*-chlorophenyl ether, allyl *p*-bromophenyl ether, 2-allyloxy-3,4-dichlorobenzoic acid, and allyl 2,4-dichlorophenyl ether underwent the normal type of ortho rearrangement. They also reported that allyl 1-propenyl-4,6-dichlorophenyl ether would undergo the expected reaction if carefully heated *in vacuo*, but at normal pressure it evolved hydrogen chloride to yield a tar.

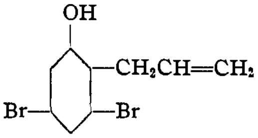
Raiford and Howland[3] reported no rearrangement with allyl 3,5-dibromophenyl ether, allyl 2,6-dibromophenyl ether, or allyl pentabromophenyl ether, but they listed no experimental details. Von Braun, Kuhn and Weismantel[4] reported a 30% yield of rearrangement product from $\beta$-bromoallyl phenyl ether when heated in decalin.

The present work was done to see if all halogen-substituted allyl aryl ethers could be fitted into the picture as drawn on the basis of results with non-halogen ethers. Out of twelve such ethers pyrolyzed, only three gave the products expected. These three, namely, allyl *o*-bromophenyl ether, allyl 3,5-dibromophenyl ether and allyl 2,4-dibromophenyl ether, are reported in this paper. The others, including von Braun's $\beta$-bromoallyl phenyl ether, are to be reported in a later communication.

Allyl *o*-bromophenyl ether rearranged smoothly and exothermally to give an 82% yield of the rearrangement product, 2-allyl 6-bromophenol. This phenol could not be made to give a chloroacetic acid derivative. Contrary to the experience of Raiford and Howland, we found that allyl 3,5-dibromophenyl ether (A) rearranged readily on heating. No difficulty was experienced in causing a smooth, exothermal rearrangement to 2-allyl-3,5-dibromophenol (B) but no chloroacetic acid derivative of this phenol could be formed. Besides this phenol, a neutral product, which was (C) 2-methyl-4,6-dibromocumarane (or possibly 5,7-dibromochromane (D)), was isolated in 6% yield. The formation of this substance would take place by ring closure of the above phenol.



(A)



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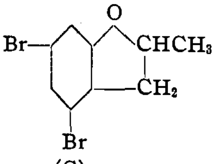

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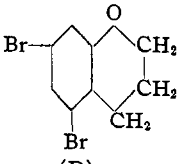

(D)

Allyl 2,4-dibromophenyl ether reacted exothermally if heated alone but the products were not satisfactory. When heated in tetralin, the exothermic reaction was not noticeable and the products were more satisfactory. The principal product was the isomer, 2-allyl-4,6-dibromophenol, which was obtained in 69% yield. This phenol did give a chloroacetic acid derivative, although in poor yield, when the method of Koelsch[5] was applied. None of these ethers evolved any gas such as allene or hydrogen bromide, or any low-boiling liquid such as diallyl or allyl bromide during the course of the decomposition.

## Experimental

### Preparation of Intermediates

3,5-Dibromophenol was prepared by the method of Kohn and Fink[6] wherein pentabromophenol is heated with ten moles of aluminum chloride in dry benzene for three hours. From 148 g. of pentabromophenol, there was obtained 61 g. (80% yield) of material of b. p. 274–278° and m. p. 78–81°. Pentabromophenol was prepared according to the method of Raiford and Howland,[3] from phenol and excess bromine in the presence of 1% of aluminum. *o*-Bromophenol and 2,4-dibromophenol were synthesized by methods in the literature.[7]

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[1] Claisen, *Ber.*, **45**, 3157 (1912).

[2] Claisen and Eisleb, *Ann.*, **401**, 21 (1913); Claisen, *ibid.*, **418**, 69 (1919); Claisen and Tietze, *ibid.*, **449**, 81 (1926).

[3] Raiford and Howland, THIS JOURNAL, **53**, 1051 (1931).

[4] Von Braun, Kuhn and Weismantel, *Ann.*, **449**, 264 (1926).

[5] Koelsch, THIS JOURNAL, **53**, 304 (1931).

[6] Kohn and Fink, *Akad. Wien. Sitzungsberichte*, **132**, 169 (1923); *Monatsh.*, **44**, 188 (1924).

[7] Meldola and Streatfield, *J. Chem. Soc.*, **73**, 685 (1898); Hewitt, Kennet and Silk, *ibid.*, **85**, 1227 (1904).

### Preparation of the Ethers

The general method of Claisen was used, in which a phenol, an alkenyl halide, anhydrous potassium carbonate and acetone were heated together. The method was modified by using an excess of allyl bromide (1.1–1.3 moles for each mole of the bromophenol), by using an excess of potassium carbonate (1.4–1.9 moles), by stirring as much as possible, by longer periods of heating and by distilling off most of the acetone before dissolving the products in a mixture of ether and water. The various runs were of 0.2–0.5 mole size and the volume of acetone taken was 200–250 cc. The yields of the three ethers varied between 85–94%.

Allyl *o*-bromophenyl ether (I) was collected at 130–134° (20 mm.); $n^{20}$D 1.5645.

*Anal.* Calcd. for $C_9H_9OBr$: Br, 37.53. Found: Br, 37.65.

Allyl 3,5-dibromophenyl ether (II), previously made by Raiford and Howland,[3] was collected at 116–122° (1 mm.); $n^{20}$D 1.5923.

Allyl 2,4-dibromophenyl ether (III) distilled at 127–134° (0.5 mm.); $n^{20}$D 1.5988.

*Anal.* Calcd. for $C_9H_8OBr_2$: Br, 54.77. Found: Br, 55.37.

### Pyrolyses

The ethers were placed in small two-necked flasks which were heated for ninety to one hundred minutes by oil-baths at 210–220°. The temperatures of the bath and the ether were read at regular intervals. In all cases a sudden exothermic reaction was encountered when the temperature of the ether was about 220°. The maximum temperature attained with II (37-g. sample) was 270°, whereas that with I (53 g.) or III (20 g.) was 241–243°. When III (51 g.) was diluted with tetralin (55 g.) and heated for two hours at 213–221°, the exothermic reaction was not apparent.

Ordinarily the pyrolysis was done in an atmosphere of nitrogen or carbon dioxide. The flask was fitted with an upright condenser. Arrangements were made to condense any low boiling liquid which might pass through the reflux condenser, to quantitatively absorb any hydrogen bromide in standard alkali, and to collect any other gas which might be evolved. The product was dissolved in ether and separated into phenolic and non-phenolic portions by extraction with alkali. The separate portions were purified in the usual manner. In all three cases, tarry materials comprised the residues from the vacuum distillation of both the phenolic and non-phenolic portions. No hydrogen bromide or other gas was evolved from any of these ethers.

**2-Allyl-6-bromophenol.**—Five per cent., or 2.7 g., of allyl *o*-bromophenyl ether (I) was recovered. The principal product was 43.9 g. (82% yield) of a colorless phenolic oil of b. p. 88–92° (2.5 mm.), $n^{20}$D 1.5708. Analysis of a redistilled product, b. p. 87–88° (2 mm.), $n^{20}$D 1.5706, showed that the product was 2-allyl-6-bromophenol.

*Anal.* Calcd. for $C_9H_9OBr$: Br, 37.52. Found: Br, 37.49.

**2-Allyl-3,5-dibromophenol.**—After heating, none of the allyl 3,5-dibromophenyl ether was recoverable. Both phenolic and neutral products were obtained. Twenty-seven grams (72%) of a colorless phenolic distillate was collected at a distillation temperature of 152–159° (2 mm.), $n^{20}$D 1.6145. The residue was a tar. Redistillation gave pure 2-allyl-3,5-dibromophenol; b. p. 138–139° (2 mm.), $n^{20}$D 1.6162. This phenol turned brown on standing.

*Anal.* Calcd. for $C_9H_8OBr_2$: Br, 54.77. Found: Br, 54.70.

**2-Methyl-4,6-dibromocumarane.**—The neutral distillate from the pyrolysis of this ether weighed 2.24 g. (6% yield); b. p. 143–147° (1 mm.), $n^{20}$D 1.6083. Analysis was satisfactory for 2-methyl-4,6-dibromocumarane.

*Anal.* Calcd. for $C_9H_8OBr_2$: Br, 54.77. Found: Br, 54.32.

**2-Allyl-4,6-dibromophenol.**—When allyl 2,4-dibromophenyl ether was heated without a solvent, results were unsatisfactory. When pyrolyzed in tetralin, 5% of the ether was recovered. The principal product (A) was 35.4 g. (69.1% yield) of a colorless, phenolic oil which darkened on standing; b. p. 118–122.5° (1 mm.), $n^{20}$D 1.6074. An additional 5.8 g. (11.2%) of lower-boiling phenolic material (b. p. 109.5–118° (1 mm.), $n^{20}$D 1.6064) was also obtained. Analysis of (A) was reasonably satisfactory for 2-allyl-4,6-dibromophenol.

*Anal.* Calcd. for $C_9H_8OBr_2$: Br, 54.77. Found: Br, 55.07.

**2-Allyl-4,6-dibromophenoxyacetic acid** was formed in 0.1 g. yield from 1 g. of 2-allyl-4,6-dibromophenol by application of the method of Koelsch.[5] About 0.03 g. was obtained which melted at 115–117.5° and 0.07 g. was less pure (m. p. 114–116.5°). It was necessary to use the latter for the neutral equivalent, which may account for the high value obtained.

*Anal.* Subs. 0.0866 g., NaOH, 29.26 cc. of 0.00796 *N*. Calcd. for $C_{11}H_{10}O_3Br_2$: neut. equiv., 350. Found: neut. equiv., 371.

## Summary

Allyl *o*-bromophenyl ether rearranged smoothly and exothermally to give 2-allyl-6-bromophenol. Allyl 3,5-dibromophenyl ether also rearranged smoothly to produce 2-allyl-3,5-dibromophenol and a small amount of a heterocyclic isomer, presumably 2-methyl-4,6-dibromocumarane. Allyl 2,4-dibromophenyl ether rearranged when heated in tetralin to give 2-allyl-4,6-dibromophenol. This gave a chloroacetic acid derivative.

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