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

The Effect of Halogen Substituents on the Rearrangement of Allyl Aryl Ethers. II. Ethers which Behave Abnormally

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The previous paper[1] of this series dealt with three halogen-substituted allyl aryl ethers which rearranged normally into allylphenols. Eleven related compounds, nine ethers and two phenols, are taken up in this paper. The list is given in Table I.

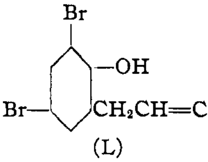
TABLE I

COMPOUNDS STUDIED

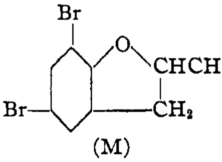
Symbol	Name	Formula
A	Allyl 2,4,6-tribromophenyl ether	$\mathrm{CH_2{=}CHCH_2{-}O{-}C_6H_2Br_3}$
B	Allyl 2-methyl-4,6-dibromophenyl ether	$\mathrm{CH_2{=}CHCH_2{-}O{-}C_6H_2MeBr_2}$
C	Allyl 2,6-dibromophenyl ether	$\mathrm{CH_2{=}CHCH_2{-}O{-}C_6H_3Br_2}$
D	Allyl 2-methyl-6-bromophenyl ether	$\mathrm{CH_2{=}CHCH_2{-}O{-}C_6H_3MeBr}$
E	β-Chloroallyl phenyl ether	$\mathrm{CH_2{=}CCl{-}CH_2{-}O{-}C_6H_5}$
F	β-Bromoallyl phenyl ether	$\mathrm{CH_2{=}CBr{-}CH_2{-}O{-}C_6H_5}$
G	γ-Chloroallyl phenyl ether	$\mathrm{CHCl{=}CHCH_2{-}O{-}C_6H_5}$
H	γ-Chloroallyl *p*-tolyl ether	$\mathrm{CHCl{=}CHCH_2{-}O{-}C_6H_4CH_3}$
I	γ-Bromoallyl phenyl ether	$\mathrm{CHBr{=}CHCH_2{-}O{-}C_6H_5}$
J	*o*-(β-Chloroallyl)-phenol	$\mathrm{HO{-}C_6H_4{-}CH_2CCl{=}CH_2}$
K	*o*-(γ-Chloroallyl)-phenol	$\mathrm{HO{-}C_6H_4{-}CH_2CH{=}CHCl}$

The results show that none of the nine ethers rearranges in the normal fashion. All give greater or less amounts of hydrogen halide and polymeric products. No C_3- or C_6-hydrocarbons were liberated, a matter of some significance[2] with A and B. Differing from the three ethers mentioned in the previous paper, none of the ethers A-D possessed unsubstituted ortho positions but C and D possessed available para positions. Therefore, they might be expected to give normal rearrangement products. Actually D did rearrange in part to 2-methyl-4-allyl-6-bromophenol. In the case of C, the phenolic mixture which was obtained seemed to be a mixture of 4-allyl-2,6-dibromophenol[3] and 2-allyl-6-bromophenol but it could not be separated satisfactorily.

That the ortho bromine may be replaced by the incoming allyl group was definitely established with the tribromo ether (A) since 2-allyl-4,6-dibromophenol (L) was a reaction product. An isomeric product, probably 2-methyl-5,7-dibromocumarane (M), was also isolated. It will be recalled that none of it was formed from allyl 2,4-dibromophenyl ether during pyrolysis[1] in spite of the large yield of L, but in this case hydrogen bromide was absent. With hydrogen bromide present the change, in part, of L into M would be anticipated.[4] The rearrangement of L into M by hydrogen bromide was confirmed by experiment. The transformation of A into L involves a dehydrogenation of the solvent or reactant: (A) + 2H ⟶ (L) + HBr.

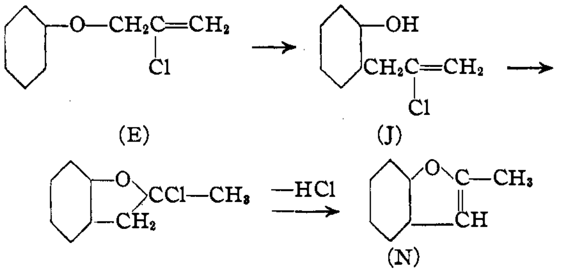


(L)



(M)

The haloallyl aryl ethers (E-I) apparently underwent rearrangement as an initial effect but only with E was the isomeric phenol (J) isolable. In this case also much of it isomerized to 2-methylcumarone (N). Part of the N polymerized but the fact that some of it was isolable was due to its comparative dilution, since when pure



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[1] Hurd and Webb, THIS JOURNAL, **58**, 941 (1936).

[2] Claisen and Tietze, *Ann.*, **449**, 81 (1926), reported such hydrocarbons from an allyl 2,4,6-trialkylphenyl ether.

[3] Raiford and Howland, THIS JOURNAL, **53**, 1051 (1931), reported non-rearrangement of (C) but they included no details.

[4] For similar ring-closures, see Claisen and Tietze, *Ber.*, **58**, 280 (1925).

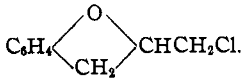
TABLE II

PROPERTIES OF THE ETHERS

Ether	B. p. °C.	B. p. mm.	$n^{20}\text{D}$	Analyses, % Halogen	Analyses, % Calcd.	Analyses, % Found	Moles of HX envolved per mole of ether
A	—	—	(*a*)	Br	64.67	64.72	0.74
B	137–141	4	(*b*)	Br	52.26	52.40	.58
C	112–113	2	1.5830	Br	—	—	.62
D	81–85	0.5	1.5451	Br	35.22	35.68	.15
E	89–91	12	1.5329	Cl	21.04	21.28	.54
F	83–88	7	1.5557	Br	—	—	.39
G	122–127	27	1.5421	Cl	21.04	21.15	.24
H	101–106	7	1.5360	Cl	19.42	19.41	.44
I	101–103	7	1.5620	Br	37.52	37.68	.03

[a] M. p. 76–77°. [b] M. p. 34–37°.

J was pyrolyzed only the polymers were found. Considerable search was made for *o*-(β-bromoallyl)-phenol from F but none was found, contrary to von Braun.[5] Complex phenols were found in 18–29% yields and also neutral polymers but phenol itself was the only phenol actually isolable. The N formed from G contained a persistent chlorine-containing impurity. It was formed normally *via* *o*-(α-chloroallyl)-phenol, and not *via* K. On heating, the chief reaction of K was isomerization to 2-(chloromethyl)-cumarane,



$C_6H_4\langle O, CH_2 \rangle CHCH_2Cl$.

Significant amounts of phenol and 1,3-dibromopropene were formed from (I), evidently by reaction of the liberated hydrogen bromide on the unused ether: $C_6H_5OCH_2CH{=}CHBr + HBr \longrightarrow C_6H_5OH + BrCH_2CH{=}CHBr$.

Experimental Part

Eastman 2,3-dibromopropene and tribromophenol were used in this work. The 2-methyl-6-bromophenol[6] was generously supplied by Dr. R. C. Huston of Michigan State College. It was redistilled before use: b. p. 204–207° (742 mm.). The 1,3-dibromopropene,[7] 2,6-dibromophenol[8] and 2-methyl-4,6-dibromophenol[8] were prepared by methods described in the literature; the percentage yields, respectively, were 23, 35 and 82.

2,3-Dichloropropene.—Although this is not new, there are no satisfactory directions for its preparation. It was found that the excellent directions for 2,3-dibromopropene[9] were adaptable. The following procedure, out of several tried, gave the best results. A mixture of 144 g. of trichloropropane, 13 g. of water and 90 g. of crushed (not powdered) sodium hydroxide was placed in a 500-cc. round-bottomed flask under a 3-ball Snyder floating-ball column. The mixture was heated with a smoky flame at such a rate that slow distillation took place. The distillate was washed with water, dried and fractionated through the column. That portion which was collected at 92.5–97° weighed 86 g. (80% yield). Redistillation gave these constants: b. p. 93–96°, $n^{21}\text{D}$ 1.4600.

Trichloropropane.—Several modifications of the directions of Pfeffer and Fittig[10] were used. Distilled glycerol dichlorohydrin (b. p. 170–176°) was used instead of the crude material. After treatment of this with phosphorus pentachloride most of the phosphorus oxychloride was distilled off before washing the product with water. From 170 g. of dichlorohydrin, 110 g. of trichloropropane (57% yield) was obtained; b. p. 153–158°.

1,3-Dichloropropene.—This was made by the method of Hill and Fischer[11] but in much lower yields. The best yield obtained was 34% for material boiling at 106–109°, or 39% for material boiling at 106–112°. Much larger amounts of trichloropropane and recovered glycerol dichlorohydrin were obtained than Hill and Fischer reported. Also, there was 60–65 g. of a high-boiling residue from 330 g. of dichlorohydrin.

Preparation of the Ethers

The ethers were prepared as before.[1] In the case of the chloroallyl and bromoallyl ethers, the limiting factor for yield was the dihalopropene rather than the phenol. In these cases 1.1 moles of the phenol was used for each mole of halide. Slight modification was necessary in the case of (A). It, being a solid and insoluble in ether, was worked up by solution in chloroform, and was recrystallized therefrom for purification.

In the synthesis of B, dibromo-*o*-cresol acted peculiarly. When the potassium carbonate was added to it in acetone solution, the mixture warmed, a gas was evolved and a sticky, brown precipitate formed. After the subsequent nine hours of refluxing with allyl bromide, much of the latter was unused. The yield of ether was very low and there was much tar.

Ethers A,[12] C,[3] F,[5] G[13] and H[13] have been made previously and analyzed. Ether A was prepared in a 0.7-mole run, and E in a 1.0-mole run. The other runs were 0.2–0.5 molar. The percentage yields, respectively, for the various ethers (A to I) were: 91, 11, 91, 77, 60, 85, 72, 65, 77. The constants and analytical data are summarized in Table II.

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(5) Von Braun, Kuhn and Weismantel, *Ann.*, **449**, 264 (1926).

(6) Huston and Neeley, THIS JOURNAL, **57**, 2177 (1935).

(7) Von Braun and Kuhn, *Ber.*, **58**, 2170 (1925).

(8) Zincke and Hedenström, *Ann.*, **350**, 273 (1906).

(9) Lespieau and Bourguel, *Organic Syntheses*, **5**, 49 (1925).

(10) Pfeffer and Fittig, *Ann.*, **135**, 359 (1865).

(11) Hill and Fischer, THIS JOURNAL, **44**, 2582 (1922).

(12) Varda, *Gazz. chim. ital.*, [2] **23**, 495 (1893); Raiford and Birosel, THIS JOURNAL, **51**, 1776 (1929).

(13) Bert, *Compt. rend.*, **192**, 1565 (1931).

Pyrolyses

The apparatus and procedure were the same as described in the previous paper.[1] Experiments were performed at 200–220°, usually for two hours. Ethers E and H were heated without solvents, ethers A, F, G, I both with and without solvents (tetralin, decalin, fluorene), and ethers B, C, D only with solvents. The HX evolved was absorbed in 0.5 *N* alkali. Solvents, in the case of A, F, G, I, did not affect the quantity of hydrogen halide evolved (see Table II). An exothermic reaction was noticed only in the case of A, but the other allyl ethers (B, C, D) might have behaved similarly had no solvent been present. The maximum temperature attained on a 25-g. sample of A, heated by a bath at 202–223°, was 270°. The inside temperature of the chloro- or bromoallyl ethers (E-I) always lagged below the bath temperature.

In all the runs, phenolic and neutral tars were produced. Also, from A, C, and D a liquid product was formed in traces which appeared to be allyl bromide. A similar product, namely, 1,3-dibromopropene, was formed in greater quantity from (I). Results with the various ethers will be listed.

Allyl 2,4,6-Tribromophenyl Ether.—A 25-g. portion of the ether was heated for two hours at 197–211° in 63 g. of tetralin. The principal phenolic product distilled at 125–130° (2 mm.); 13.5 g., 68% yield. It was essentially 2-allyl-4,6-dibromophenol. When treated with chloroacetic acid it gave 2-allyl-4,6-dibromophenoxyacetic acid,[1] m. p. 114–116°.

The neutral fraction weighed 6.6 g., about half of which was 2-methyl-5,7-dibromocumarane, b. p. 130–135° (1 mm.). This was synthesized for comparison. When (A) was heated without a solvent, the only identifiable product was a small amount of tribromophenol.

2-Methyl-5,7-dibromocumarane.—A sample of 2-allyl-4,6-dibromophenol was boiled for two hours with an aqueous acetic acid solution of hydrogen bromide according to Claisen's general method.[4] The cumarane (M) was collected in 47% yield at 129–134° (1 mm.); $n^{20}\text{D}$ 1.6075.

Anal. Calcd. for $C_9H_8OBr_2$: Br, 54.77. Found: Br, 54.75.

Allyl 2-Methyl-4,6-dibromophenyl Ether.—Sixteen grams of (B), mixed with 24 g. of tetralin and heated for two hours, yielded 5.5 g. of phenolic products and 8.1 g. of neutral material. No pure products were isolable from the fractions.

Allyl 2,6-Dibromophenyl Ether.—From 47 g. of (C), heated with 66 g. of tetralin, there was isolated 17.2 g. of crude phenolic material. Distillation at 2 mm. gave these fractions (°C., g., $n^{20}\text{D}$, % Br): 96–98, 2.9, 1.5784, 39.97; 98–104, 6.2, 1.5842, (no anal.); 107–112, 2.4, 1.5953, 44.61; 112–117, 2.3, 1.6057, 46.14; residue, 3 g. The lowest fraction appeared to be chiefly 2-allyl-6-bromophenol (calcd. Br, 37.54), and the highest fraction chiefly 4-allyl-2,6-dibromophenol (calcd. Br, 54.77).

Distillation of the neutral products at 1–2 mm. yielded 3 g. of naphthalene (formed by dehydrogenation of the tetralin), and 7.4 g. of the recovered ether, b. p. 102–112°.

Allyl 2-Methyl-6-bromophenyl Ether.—Thirty-three grams of (D), mixed with 33 g. of tetralin, yielded 7.7 g. (23%) of 2-methyl-4-allyl-6-bromophenol; b. p. 101–110° (1.5 mm.), $n^{20}\text{D}$ 1.5711.

Anal. Calcd. for $C_{10}H_{11}OBr$: Br, 35.2: Found: Br, 35.3.

Evidence was obtained for about 1 g. of 2-methyl-6-bromophenol but there was no evidence for 2-methyl-6-allylphenol, which would be anticipated if there were replacement of the bromine in (D) as in (A). No pure products were isolated from the 14.2 g. of crude neutral material.

β-Chloroallyl Phenyl Ether.—When heated for two hours at 216–223°, this ether (52 g.) yielded a colorless phenolic oil (12.4 g.) which boiled at 130–134° (12 mm.); $n^{20}\text{D}$ 1.5778. Analysis showed this to have the composition of *o*-(β-chloroallyl)-phenol. When allowed to stand, this material gradually became viscous and finally changed to a solid.

From the neutral material, 8 g. of 2-methylcumarone was isolated; b. p. 190–193°, b. p. 56–57° (8 mm.), $n^{20}\text{D}$ 1.5590.

Anal. Calcd. for C_9H_8O: C, 81.8; H, 6.06. Found: C, 81.4; H, 6.21.

This material reacted with bromine in carbon disulfide to give an oil; b. p. 116–119° (15 mm.); $n^{20}\text{D}$ 1.5873. 2-Methylcumarone (b. p. 190–193°, $n^{25}\text{D}$ 1.5552) and its bromination product (b. p. 114–118° (15 mm.); $n^{20}\text{D}$ 1.5875) were prepared for comparison by the method of Adams and Rindfusz.[14]

β-Bromoallyl Phenyl Ether.—When this ether was heated without a solvent, only a tar resulted. When 15 g. of (F) was heated with 3 g. of decalin or 5 g. of fluorene, 2–3 g. of a bromine-containing, infusible solid resembling carbon accumulated on the sides of the flask. Considerable phenolic substances (18–29%) were extracted from the reaction mixture. Distillation gave rise to a trace of phenol, identified as tribromophenol. Nothing distilled at 135° (14 mm.), the b. p. of *o*-(β-bromoallyl)-phenol. The residue was a tar.

Less than 1 g. of (F) was recovered on attempted distillation of the neutral material. The thick tarry residue weighed 3.5 g.

γ-Chloroallyl Phenyl Ether.—Fourteen different runs were carried out with (G). Practically no phenolic products were obtained except in the runs with fluorene as solvent. Thus, from 31–33 g. of G (in 11–14 g. of fluorene), heated for forty, ninety and four hundred forty minutes, there was formed 0.5, 1.2 and 2.3 g. of phenols. The 0.5 and 1.2-g. portions were thick, dark oils which gave good chlorine tests. The 2.3-g. portion yielded 0.53 g. of phenol (identified as tribromophenol) on steam distillation.

The principal product from (G) was a neutral material of lower b. p. It could not be separated completely from unchanged G either by vacuum distillation or by chemical means. On distillation at atmospheric pressure, it polymerized. Data from two runs will be listed, with and without a solvent.

Without Solvent.—In this run, 30.8 g. of G, $n^{21}\text{D}$ 1.5424, was heated for three hours at 215–225°, then distilled at 27 mm. (°C., g., $n^{21}\text{D}$): 103–112, 0.5, 1.5606; 112–115, 3.5, 1.5598; 115–118, 3, 1.5573; 118–120, 4, 1.5493; dark residue, 17 g. The 3.5-g. fraction (112–115°) possessed a

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[14] Adams and Rindfusz, THIS JOURNAL, **41**, 648 (1919). See also Claisen, *Ann.*, **418**, 84 (1919); *Ber.*, **53**, 322 (1920).

refractive index 0.0174 higher than G. Analysis (Cl, 12.8%) indicated 39.4% of chlorine-free material.

With Solvent.—In this run, 30.8 g. of G, $n^{23}\text{D}$ 1.5392, admixed with 11.5 g. of fluorene, was heated at 250–255° for forty minutes. From it there was collected at 9 mm. about 23 g. of distillates (°C., g., $n^{23}\text{D}$). 68–74, 1.9, 1.5718; 74–77, 3.3, 1.5657; 78–82, 5.0, 1.5572; 83–85, 8.7, 1.5468; 85–88, 4.8, 1.5437. The residue, nearly colorless, was chiefly fluorene. None of the fractions, in common with G, possessed activity toward alcoholic or ammoniacal silver nitrate. This and other evidence suggests that the chlorine-containing impurity in the fractions is (G). The 1.9-g. fraction (68–74°) possessed a refractive index 0.0326 higher than the original ether. Analysis (Cl, 7.72%) indicated 63.3% of chlorine-free material.

γ-Chloroallyl *p*-Tolyl Ether.—From 25 g., only 0.3 g. of phenolic material was found. In the neutral portion, 10.4 g. of (H) was recovered. There was 10.8 g. of a black residue the mol. wt. of which, determined cryoscopically in benzene, was 424. This suggests a trimer of 2,5-dimethylcumarone (mol. wt., 438).

γ-Bromoallyl Phenyl Ether.—From 18.9 g. of (I), the most interesting neutral material was 1.41 g. of liquid, b. p. 157°, which was satisfactory for 1,3-dibromopropene. About 27% of (I) was recovered. The neutral tar weighed 2 g. The only recognizable phenolic product from this ether was phenol itself, formed in 9–18% yields.

The *o*-Chloroallylphenols

o-(β-Chloroallyl)-phenol (J), b. p. 95–100° (1 mm.), 130–134° (12 mm.), was a product of pyrolysis of β-chloroallyl phenyl ether (E).

Anal. Calcd. for C_9H_9OCl: Cl, 21.04. Found: Cl, 21.02.

o-(γ-Chloroallyl)-phenol (K) was prepared in 17% yield by reaction of 47 g. of phenol, 11.5 g. of fine sodium, 250 cc. of dry benzene and 56 g. of 1,3-dichloropropene for seventeen hours. The first half of the reaction was performed at room temperature, the last half at refluxing temperature. On working up the products (alkali-extraction and vacuum distillation), 14.5 g. of (K) was obtained; b. p. 151–156° (31 mm.), $n^{23}\text{D}$ 1.5638. Concurrently, 4.5 g. of the isomeric ether (G) was obtained from the alkali-insoluble portion. The phenol (K) was analyzed.

Anal. Calcd. for C_9H_9OCl: Cl, 21.04. Found: Cl, 21.05.

Pyrolyses.—Phenols J and K were heated without solvents in the manner described above for the ethers. The hydrogen chloride evolved from J was 0.73 mole (per mole of J) during ninety minutes, whereas that from K was only 0.023 mole during two hundred minutes.

Approximately equal amounts of molasses-like phenolic and neutral products were formed from J. The phenolic material gradually became quite hard and resinous. There was 54% recovery of K. From a 6-g. run, the principal product was 1.03 g. of a neutral, halogen-containing material; b. p. 106–108° (9 mm.), $n^{23}\text{D}$ 1.5595. Analysis and comparison with synthetic material showed it to be 2-(chloromethyl)-cumarane.

Anal. Calcd. for C_9H_9OCl: Cl, 21.04. Found: Cl, 20.15.

Synthetic 2-(Chloromethyl)-cumarane.—Five grams of K, mixed with 20 cc. of acetic acid and 10 cc. of 48% hydrobromic acid, was heated for two hours. This is Claisen's method[4] of ring-closure. There was 2.3 g. of K recovered. From the neutral material, 1.5 g. of the desired cumarane was collected between 140–155° (28 mm.), two-thirds of which was collected at 145–155°. This fraction, $n^{24}\text{D}$ 1.5615, was analyzed.

Anal. Calcd. for C_9H_9OCl: Cl, 21.04. Found: Cl, 20.94.

Summary

Allyl aryl ethers were prepared wherein the aryl groups were 2-methyl-6-bromophenyl, 2,4-dibromophenyl, 2-methyl-4,6-dibromophenyl and 2,4,6-tribromophenyl. Also, "allyl" phenyl ethers were synthesized wherein the "allyl" group represented β- and γ-chloroallyl, β- and γ-bromoallyl. γ-Chloroallyl *p*-tolyl ether was also studied. All nine of these ethers evolved hydrogen halide on heating and gave rise to a complex mixture of products. The only cases which rearranged into isolable phenolic isomers were allyl 2-methyl-6-bromophenyl ether, β-chloroallyl phenyl ether and possibly allyl 2,6-dibromophenyl ether. Other phenolic products and neutral materials were formed. Cyclization was encountered in many cases and tarry polymeric products invariably were formed.

The chief organic products formed during the pyrolysis of allyl tribromophenyl ether were 2-allyl-4,6-dibromophenol and 2-methyl-5,7-dibromocumarane.

For purposes of comparison, study was also made of the pyrolysis of *o*-(β-chloroallyl)-phenol and *o*-(γ-chloroallyl)-phenol.

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