[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

THE ACTION OF BROMINE ON CERTAIN MIXED ETHERS

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Henry[1] obtained phenyl allyl ether by the action of allyl bromide on sodium phenolate, but gave no details regarding the method and recorded no yield. He noted that when bromine was brought in contact with the ether, both the allyl and the phenyl radicals reacted. However, nothing was said about the character of the product. 2,4,6-Tribromophenyl allyl ether was obtained by Varda[2] by the alkylation of the bromophenol, and Claisen and Eisleb[3] obtained 4-bromophenyl allyl ether by synthesis from *p*-bromophenol, not by bromination of the ether. Fairbourne and Toms[4] brominated 2,4-dinitrophenyl allyl ether and, as might have been predicted,[5] found that the halogen entered the allyl radical only. Colbert,[6] working in this Laboratory, noted similar behavior with 2-nitro-4-chlorophenyl allyl ether, though the amount of material available and the difficulty of purification prevented absolute identification of the product. In view of these facts, it was proposed to test the action of bromine on phenyl allyl ether under conditions where both radicals might react.

When phenyl allyl ether was treated with excess[7] of bromine it gave some 2,4,6-tribromophenol and a tetrabromo ether. The identity of the ether was established by preparing it in a different way. 2,4-Dibromophenol was converted into the corresponding allyl ether and the latter was treated with excess of bromine. The tetrabromo ether isolated in the first experiment was obtained here.

The failure to introduce more than two atoms of bromine into the phenyl radical of phenyl allyl ether under the conditions stated suggested the examination of ethers containing alkyl radicals. The methyl, ethyl and propyl ethers of 2,4,6-tribromophenol are on record, but only the

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[1] Henry, *Ber.*, **5**, 455 (1872).

[2] Varda, *Gazz. chim. ital.*, [2] **23**, 495 (1893).

[3] Claisen and Eisleb, *Ann.*, **401**, 38 (1913).

[4] Fairbourne and Toms, *J. Chem. Soc.*, **119**, 1038 (1921).

[5] It is well known that the difficulty of introducing substituents into the phenyl radical increases as the number of groups present increases, and that the ether or ester is less reactive than the corresponding phenol. This relation was emphasized in the preparation of the bromine addition product of *o*-allyl phenol by Adams and Rindfusz, THIS JOURNAL, **41**, 654 (1919), who found it necessary to protect the hydroxyl group by acetyl, to use only the calculated amount of bromine to saturate the allyl radical and to conduct the experiment at 0°.

[6] Colbert, unpublished report.

[7] More than that required to saturate the allyl radical and to substitute positions 2, 4 and 6 in the phenyl group.

first was made by bromination of the ether. In the present work, in which the ethers were allowed to remain in contact with excess of bromine for several days, it was found that, in addition to bromination of the phenyl radical, certain ethers were split by the hydrogen bromide formed. With phenyl methyl, ethyl, *n*-propyl and *iso*butyl ethers, the 2,4,6-tribromo ether[8] resulted; with 2,4,6-tribromophenyl *n*-propyl and *iso*propyl, no changes occurred, while with phenyl *iso*propyl, *sec.*-butyl[9] and *tert.*-butyl, and with 2,4-dibromophenyl *iso*propyl and to the extent of 10 and 20%, respectively, with phenyl methyl and ethyl, the 2,4,6-tribromophenol[10] was formed.

Experimental Part

A. Phenyl Allyl Ether and Substitution Products

2,4-Dibromophenyl-β,γ-dibromopropyl Ether.—Twelve g. of phenyl allyl ether[11] dissolved in 10 cc. of chloroform was treated gradually with an excess of bromine in chloroform, with cooling, the mixture allowed to stand for four days and then the solvent and excess of bromine were distilled off. Distillation under reduced pressure gave one fraction that boiled just below 190° at 5 mm. and which solidified upon standing. Crystallization from petroleum ether gave nearly colorless needles that melted at 93°.[12] A second fraction distilled at 220–223° at 10 mm., apparently with slight decomposition. This did not solidify on standing. Analysis is given in Table I.

2,4-Dibromophenyl Allyl Ether.—This was obtained in 54% yield by converting 25 g. of the corresponding dibromophenol into the ether by Claisen's general method. The product distilled between 165 and 170° at 20–22 mm. and was nearly colorless. It did not solidify upon cooling. When a chloroform solution of this product was treated with an excess of bromine, it gave the tetrabromo compound described above.

2,4,6-Tribromophenyl-β,γ-dibromopropyl Ether.—Twenty-eight g. of *s*-tribromophenyl allyl ether, m. p.[13] 75°, was dissolved in 100 cc. of chloroform, 15 g. of bromine was added slowly with cooling and the mixture allowed to stand for three days, after which the solvent and excess of bromine were distilled off under reduced pressure.

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[8] The ethyl derivative melted at 69° and is probably identical with that obtained by Purgotti [*Gazz. chim. ital.*, **16**, 528 (1886)] by treatment of the silver salt of the bromophenol with ethyl iodide, and who reported 69°, but did not analyze the product. Varda [*ibid.*, [II] **23**, 494 (1893)] used the potassium salt of the phenol and reported 72–73° for a substance that analyzed well. The product here in question was nearly pure. *Anal.* Subs., 0.1173: AgBr, 0.1840. Calcd. for $C_8H_7OBr_3$: Br, 66.83. Found: Br, 66.68.

[9] The product boiling between 100 and 108° under 40-mm. pressure, and obtained in 23% yield from phenol and secondary butyl bromide by Claisen's method, was used.

[10] Sodium acetate in the reaction mixture prevents splitting except in the case of phenyl *tert.*-butyl ether.

[11] Claisen and Eisleb, *Ann.*, **401**, 29 (1913).

[12] Repetition of this experiment showed that this fraction consisted mainly of 2,4,6-tribromophenol. The hydrogen bromide evolved in the conversion of a portion of this ether into a bromine substitution product decomposed some of it to give phenol, which was then brominated. If the bromination is conducted in the presence of sodium acetate, the splitting and consequent formation of tribromophenol can be avoided.

[13] Varda, ref. 2, recorded 77°.

Recrystallization from ligroin (40–60°) by cooling in a freezing mixture gave nearly colorless needles.

2-Nitro-4-chlorophenyl-β,γ-dibromopropyl Ether.—One g. of the corresponding nitrochlorophenyl allyl ether[14] was treated with excess of bromine in chloroform solution and allowed to stand for a few days. After removal of solvent and excess of bromine, the oily residue was held at about 98° and 20 mm. for several hours and then allowed to cool and solidify. Crystallization from petroleum ether gave colorless needles.

2,4,6-Trinitrophenyl-β,γ-dibromopropyl Ether.—Five g. of picryl allyl ether[15] was dissolved in chloroform, an excess of bromine in the same solvent added and the mixture allowed to stand for twenty-four hours. Evaporation of solvent and unchanged bromine left a colored solid which after repeated crystallization from petroleum ether gave nearly colorless prisms.

B. Phenyl Alkyl Ethers

2,4-Dibromophenyl Isopropyl Ether.—This was prepared by Claisen's method from the dibromophenol and *iso*propyl iodide, and was obtained as an oil that distilled at 156° and 18 mm.

2,4,6-Tribromophenyl Isopropyl Ether.—This was obtained in 74% yield from tribromophenol with a slight excess of *iso*propyl bromide. At 190° and 30 mm. it distilled as a faintly colored oil that solidified on standing.

TABLE I

PHYSICAL CONSTANTS AND ANALYTICAL DATA

Compound β,γ-Dibromopropyl ethers	Formula	M. p., °C.	Analyses, %		
				Calcd.	Found
2,4-Dibromophenyl-	$C_9H_8OBr_4$	Liq.	Br	70.75	70.80
2,4,6-Tribromophenyl-	$C_9H_7OBr_5$	42.5–43.5	Br	75.32	75.23
2-Nitro-4-chlorophenyl-	$C_9H_8O_3NClBr_2$	55	Hal	52.32	52.31
2,4,6-Trinitrophenyl-	$C_9H_7O_7N_3Br_2$	102[a]	Br	37.27	37.23
*Iso*propyl ethers					
2,4-Dibromophenyl-	$C_9H_{10}OBr_2$	Liq.	Br	54.42	54.37
2,4,6-Tribromophenyl-	$C_9H_9OBr_3$	40	Br	64.34	64.26

[a] After this work had been completed Fairbourne and Foster [*J. Chem. Soc.*, 3148 (1926)], published a report in which this product was assigned a melting point of 106–107°, while the allyl ether from which it was obtained melted at 90°.

Summary

1. Under the conditions of these experiments only two bromine atoms were introduced into the phenyl radical of phenyl allyl ether.

2. The hydrogen bromide evolved in the bromination of the ethers tested may split them unless sodium acetate is present. The splitting is most pronounced when the alkyl is connected through a secondary or tertiary carbon atom.

3. Further work on these derivatives is in progress.

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[14] Raiford and Colbert, THIS JOURNAL, **48**, 2658 (1926).

[15] Attempts to prepare this product by Claisen's [*Ann.*, **401**, 29 (1913)] and by Willgerodt's [*Ber.*, **12**, 765 (1879)] methods, respectively, were unsuccessful. Treatment of silver picrate with allyl bromide also failed, but substitution of the iodide gave the desired result. Extraction of the reaction mixture with petroleum ether gave a red oil which upon the addition of a little water gave a crystalline solid; m. p. 85°.