

of the present authors will pursue this investigation farther, and it is with some regret that we leave this field to other workers.

This research was carried out during the summer of 1917 at the Puget Sound Marine Station, at which time the authors were associated with the University of Washington.

Summary.

1. The existence of several per cent. of carbon monoxide in the gas contained in the Pacific Coast kelp, *Nereocystis luetkeana*, is confirmed.
2. The substance of the kelp, when ground and allowed to undergo autolysis and decay does not form carbon monoxide by enzyme action or fermentation process.
3. Kelp plants, in which the gas normally present within the floater is replaced by air, form several per cent. of carbon monoxide within a few days.
4. The formation of carbon monoxide takes place only when oxygen is present as one of the gases within the floater. No carbon monoxide is formed when the floater is filled with hydrogen or nitrogen.
5. Light does not affect the rate of formation of carbon monoxide.
6. It is concluded that the carbon monoxide is formed as a product of respiration rather than as an intermediate step in photosynthesis.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

A COMPARISON OF THE ACTIVITY OF CERTAIN UNSATURATED GROUPS WITH THE ACTIVITY OF THE ALLYL GROUP IN CERTAIN ETHERS.¹

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It has long been an established fact that the allyl group is bound only very loosely to oxygen, nitrogen, sulfur, or halogen. As examples of the mobility of the allyl group may be mentioned the ease of rearrangement of allyl thiocyanate to allyl isothiocyanate,² the great reactivity of allyl halides,³ the readiness with which the allyl group is eliminated from certain nitrogen compounds⁴ and the rearrangement of O-allyl acetoacetic ester or O-allyl acetylacetone⁵ into the corresponding C-substituted compounds. The most striking example, however, is the quantitative

¹ This communication is an abstract of work done by S. G. Powell in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² *Ber.*, 8, 464 (1875); *Ann.*, 178, 89 (1875).

³ *J. Chem. Soc.*, 97, 416 (1910).

⁴ *Ibid.*, 57, 767 (1890); 104, 39 (1913); *Ann.*, 382, 1 (1911); *Ber.*, 33, 1438, 2728 (1900).

⁵ *Ber.*, 45, 3157 (1912).

rearrangement of allyl phenyl ethers into *o*-allyl phenols.¹ This reaction has already proved itself to be a most useful one and has invited the attention of many investigators.² A theoretical explanation, however, of the activity of the allyl group has never been given.

The object of this research was to explain the phenomenal mobility of the allyl group. As the first point of attack, a determination of the exact structure which leads to such activity was undertaken and the results are described in this communication. The investigation was started by comparing other unsaturated groups with the allyl for the purpose of discovering (1) whether a C = in any other position besides the $\beta\gamma$, and (2) whether any other unsaturated linkage in the $\beta\gamma$ position, would be just as effective in producing a mobile group as a C=C in the same position. Since the rearrangement of the allyl phenyl ethers to *o*-allyl phenols merely by heating to the boiling point for a short time is such an extremely smooth reaction, the rearrangement of other unsaturated phenyl ethers was attempted. The results of this work have shown that none of the following ethers rearranges under the same conditions as the allyl phenyl ethers: $\text{ROCH}=\text{CH}_2$, $\text{ROCH}_2\text{CH}_2\text{CH}=\text{CH}_2$, $\text{ROCH}_2\text{C}\equiv\text{CH}$, ROCH_2CN , ROCH_2R ; where R stands for a phenyl or substituted phenyl group.

In a German patent³ covering allyl phenyl ether rearrangements, it is stated that the compounds, $\text{ROCH}=\text{CH}_2$, $\text{ROCH}(\text{C}_6\text{H}_5)_2$, rearrange, but no experimental details are given. It is likely that these statements were made in anticipation of what might take place, as the results of this work indicate no rearrangement in these compounds. When phenyl vinyl ether was refluxed for 12 hours there was no change. When this substance was heated in a sealed tube for 12 hours at $260\text{--}280^\circ$, there was only very slight decomposition with the formation of phenol. The *p*-tolyl-vinyl ether, upon heating in a sealed tube to 230° did, to be sure, decompose, but the chief reaction product was *p*-cresol. Moreover, heating the same compound for 2 hours at its boiling point (177°) yielded chiefly *p*-cresol along with tarry products.

The 3 substances, $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2$, $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$, $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{C}=\text{C}(\text{CH}_3)_2$, were next studied. All of them proved to be remarkably stable, for after 12 hours refluxing neither rearrangement nor decomposition had taken place.

On the other hand, phenyl-propargyl ether and *p*-bromophenyl-propargyl ether were found to be very unstable. Refluxing brought about complete decomposition within 2-3 hours, giving tarry mixtures in

¹ *Ann.*, 401, 21 (1913); 418, 69 (1919).

² *Ber.*, 48, 1716 (1915); *THIS JOURNAL*, 39, 2202 (1917); 41, 654 (1919); *Ann.*, 414, 250 (1918).

³ *D. R. P.* 268,099; *Frdl.*, 11, 181 (1912-14).

each case. Even in amyl ether (b. p. 170°) as a solvent, extensive decomposition took place. In none of the rearrangement experiments was alkali soluble material found.

Of the ethers with a C≡N linkage in the βγ position, the following were chosen for study: C₆H₅OCH₂CN and *p*-CH₃C₆H₄OCH₂CN. Although the former showed some decomposition, after 15 hours refluxing, the latter upon 24 hours heating set to a solid brittle tar. When amyl ether was used as a solvent, very little decomposition occurred, a small amount of *p*-cresol being obtained.

Finally, the benzyl ethers were investigated, and as they are very similar in structure to the allyl ethers, the expectation was that they would rearrange. Of these, benzyl-phenyl ether, benzyl-tolyl ether, and several of their nitro and bromo substitution products were studied. In no case did rearrangement take place. It was found that undoubtedly the linkage between the benzyl group and the oxygen is a weak one, but the chief products of the decomposition are not diphenylmethane, but benzene and toluene derivatives. The nitro compounds in general decompose rapidly and the bromine derivatives break down completely with the evolution of hydrobromic acid.

In connection with the study of the benzyl ethers, it is interesting to note the results which have been obtained by previous investigators on the comparative ease with which the benzyl and allyl compounds decompose or react. Clarke¹ has found by a study of the reaction between various bromides and pyridine that benzyl bromide is nearly 5 times as active as allyl bromide. On the other hand, von Braun² studying the quaternary ammonium halides discovered that in every case allyl chloride would split off in preference to benzyl chloride and both of them far more easily than alkyl or aryl chlorides. Thus it is obvious that in certain reactions the benzyl is more reactive than the allyl and in other cases less reactive. No definite results on this point were obtained by a study of the phenyl ethers.

In conclusion, the rearrangement of phenyl ethers is not a suitable reaction for the study of the comparative reactivity of various unsaturated groups. It is possible that satisfactory results can be obtained by a study of the rearrangements of derivatives of O-acetoacetic ester to C-acetoacetic ester or of the decomposition of the quaternary ammonium halides as investigated by von Braun. It is even possible that the rearrangements of the thiocyanates to isothiocyanates is a field in which various unsaturated groups may be compared.

Experimental.

Phenyl-Vinyl Ether, C₆H₅OCH = CH₂.—This substance was prepared by the action of solid sodium hydroxide upon phenyl-β-bromo-

¹ *J. Chem. Soc.*, 97, 416 (1910).

² *Ber.*, 33, 1438, 2728 (1900); *Ann.*, 382, 1 (1911).

ethyl ether.¹ It boils at 155–156°. Twenty g. of this product was refluxed for 12 hours and then distilled. No decomposition had taken place. In a second experiment, 20 g. was heated in a sealed tube at 260–280° for 12 hours. The product took on a light brown color. On distilling, most of the product boiled at 155–165° and was without question unchanged ether; a small lower fraction, less than one g., had a strong, piercing odor but was not identified, while a high-boiling fraction of about 4 g. was shown to be phenol.

***p*-Tolyl-Vinyl Ether**, $\text{CH}_3\text{C}_6\text{H}_4\text{OCH}=\text{CH}_2$.—This substance was made in a similar manner to the phenyl-vinyl ether using *p*-cresol in place of phenol. The intermediate *p*-tolyl- β -bromoethyl ether² has already been described and is a colorless crystalline solid melting at 40° and boiling at 254–255°. To prepare the vinyl ether, 100 g. of the bromo compound is mixed with 200 g. of powdered sodium hydroxide in a 500 cc. copper flask and distilled from an oil bath at 250–300°. The distillate is extracted with a small amount of ether, the ether solution dried over sodium sulfate, and then fractionated. The *p*-tolyl-vinyl ether is a colorless, mobile liquid with a pleasant odor, b. p. 177–180°, n_D^{30} 1.513, D_{25}^{30} 0.975.

Subs., 0.2504; CO_2 , 0.7370; H_2O , 0.1620.

Calc. for $\text{C}_9\text{H}_{10}\text{O}$: C, 80.6; H, 7.5. Found: C, 80.3; H, 7.2.

Twenty g. of this substance was heated for 10 hours in a sealed tube at 230°. Upon cooling, the product was a dark reddish brown, tarry substance which was dissolved in ether and this solution then extracted with 10% sodium hydroxide solution. It was found that the alkali contained a considerable portion of *p*-cresol. The alkali insoluble products were tarry in nature and no definite substance could be obtained from them. Even upon merely refluxing for 2 hours, the *p*-tolyl-vinyl ether decomposed to give *p*-cresol and high-boiling, dark-colored, alkali-insoluble material.

An attempt was made to prepare the *p*-bromophenyl-vinyl ether first by the action of alkali upon the *p*-bromophenyl- β -bromoethyl ether,³ and second by the decomposition of β -*p*-bromophenoxy-ethyl-trimethyl ammonium bromide. Neither of these methods gave the product that was desired. The *p*-bromophenyl- β -bromoethyl ether gave deep-seated decomposition upon heating with alkali.

β -*p*-Bromophenoxy-ethyl-trimethyl Ammonium Bromide, $\text{BrC}_6\text{H}_4\text{-OCH}_2\text{CH}_2(\text{CH}_3)_3\text{NBr}$.—This substance is formed by heating 56 g. of *p*-bromophenyl- β -bromoethyl ether in a sealed tube at 100° for 12 hours with excess of a methyl alcohol solution of trimethylamine. Upon

¹ *Ber.*, 43, 2178 (1900).

² *Ibid.*, 24, 189 (1891).

³ *J. Biol. Chem.*, 21, 439 (1915).

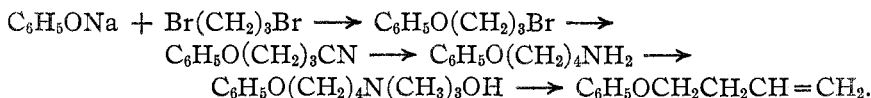
cooling, the contents of the tube are a mass of white crystals which are washed with dry ether to extract unchanged *p*-bromophenyl- β -bromoethyl ether. The quaternary ammonium compound is purified by dissolving in absolute methyl alcohol and reprecipitating with absolute ether.

Subs., 0.9466; 28.5 cc. 0.1 *N* AgNO₃.

Calc. for C₁₁H₁₇ONBr: Br, 23.6. Found: 24.0.

This substance is treated with excess of silver oxide in water solution, the silver bromide filtered and the solution evaporated to a small volume on a water bath. The sirupy residue is then distilled with a free flame but from the distillate no constant boiling fraction is obtained.

Phenoxy-4-Butene-1, C₆H₅OCH₂CH₂CH=CH₂.—This ether has been prepared by the method of Braun¹ by the following series of reactions:



The γ -phenoxypropyl bromide is readily made from the sodium phenylate and trimethylene bromide² and can be obtained in 65% yields. This readily forms the cyanide in 75% yields.³ The nitrile by the action of absolute alcohol and sodium gives 72% yields of amine hydrochloride⁴ which with alkali gives free base. To convert the amine into the quaternary ammonium iodide, then the hydroxide, and finally the ethylene compound, 70 g. is dissolved in one liter of methyl alcohol and mixed with a solution of 75 g. of sodium hydroxide in 200 cc. of water. To this mixture 216 g. of methyl iodide is added slowly. Too rapid addition of the iodide will result in a large portion of the material being thrown out of the top of the condenser. The mixture is refluxed for 8 hours, then allowed to cool when the quaternary ammonium iodide separates out in shining flakes, m. p. 168°. From 77 g. of the quaternary ammonium iodide in 300 cc. of water, and an excess of silver oxide, a solution of the corresponding quaternary ammonium hydroxide is obtained. This is filtered from the silver iodide and evaporated almost to dryness on the water bath, then distilled in a small distilling flask with a free flame. The distillate consists of phenoxy-4-butene-1 and γ -phenoxy-butyl-dimethylamine. By shaking the distillate with ether and then with dil. hydrochloric acid to extract the amine, an ether solution of the ethylene compound is obtained. This is dried over sodium sulfate, the ether removed and the residue fractionated. A colorless liquid, b. p. 209°, is produced.

¹ *Ann.*, 382, 34 (1911); *Ber.*, 44, 3699 (1911).

² *Ber.*, 24, 2631 (1891).

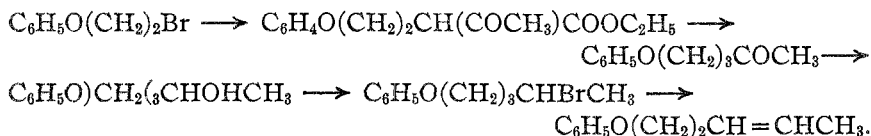
³ *Ibid.*

⁴ *Ibid.*, 24, 3231 (1891); 39, 4119 (1906).

The γ -phenoxy-butyl-dimethylamine may be used over again for the production of the quaternary ammonium iodide.

Twenty g. of phenoxy-4-butene-1 was refluxed for 48 hours. The temperature remained constant at 209° and a distillation showed that no decomposition had taken place. Even after heating in a sealed tube for 5 hours. at $250\text{--}270^\circ$ no decomposition took place.

Phenoxy-5-Pentene-2, $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$.—This substance has already been prepared by the action of the sodium phenylate upon 1,4-dibromo-pentane.¹ Since, however, the dihalide is a difficult substance to obtain, a new method was used for the synthesis. This consisted in the following series of reactions:



Phenyl- β -bromoethyl ether was prepared by the method described in the literature with slight modifications.² In a 5-liter flask fitted with an upright condenser, 660 g. (3.5 moles) of ethylene dibromide, 280 g. (3 moles) of phenol, and 1000 cc. of water were heated to boiling. To this mixture was added in portions of 25 cc. every half hour 500 cc. of 4 *N* sodium hydroxide solution (2 moles); after all the alkali had been added, the mixture was heated 2 hours longer. Upon cooling, the lower oily layer was separated, washed with dil. sodium hydroxide solution and distilled. As soon as the ethylene dibromide had come over, the remainder of the material was distilled under diminished pressure and the fraction boiling $130\text{--}145^\circ$ at 25 mm. collected. It solidified to a mass of white crystals, m. p. 33° , and amounted to 225 g. (55% yield). The bromide was next condensed with sodium acetoacetic ester and the resulting compound split to the ketone.³ The ketone was then reduced to the alcohol.

γ -Phenoxy-propyl-methyl Carbinol, $\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_3\text{CHOHCH}_3$.—A solution of 36 g. of γ -phenoxy-propyl-methyl ketone in 300 cc. of ether is added to 250 g. of sodium hydrogen carbonate mixed with 1000 cc. of water. The whole is cooled with ice and then 60 g. of sodium is added in small portions over a period of 36 hours, keeping the mixture cold at all times. When all of the sodium has been used up, the ether layer is separated, washed with a saturated solution of sodium hydrogen sulfite to

¹ *J. Russ. Phys. Chem. Soc.*, 30, 826 (1898).

² *Ber.*, 43, 2178 (1900).

³ The condensation of phenyl- β -bromoethyl ether with acetoacetic ester and then subsequent decomposition to the corresponding ketone has been carried out in this laboratory in a research under the direction of Dr. Oliver Kamm. The details for the production of these compounds and their physical constants will be published in a communication soon to appear.

remove any unreduced ketone and dried over sodium sulfate. The ether is distilled off on the water bath and the residue fractionated under diminished pressure. The portion boiling 160–165° at 20 mm. is collected and upon redistillation gives 27 g. (75% yield) of a colorless, viscous oil, boiling at 163° at 20 mm., n_D^{25} 1.5123, D_{25}^{31} 1.025.

Subs., 0.3132, 0.2832; CO₂, 0.8376, 0.7560; H₂O, 0.2672, 0.2276.

Calc. for C₁₁H₁₈O: C, 73.3; H, 8.9. Found: C, 73.0; 72.8; H, 9.5, 8.9.

Phenoxy-5-bromo-2-pentane, C₆H₅O(CH₂)₃CHBrCH₃.—36 g. of γ -phenoxy-propyl-methyl carbinol is well cooled with ice and treated with 30 g. of phosphorus tribromide. After the addition, the mixture is refluxed for 30 min. to complete the reaction and then poured into ice water. The oily layer is taken up with ether, the ether solution washed with dil. sodium hydroxide, then with water and finally dried over sodium sulfate. The ether is distilled off on the water bath and the residue fractionated under diminished pressure. The crude fraction distilling at 165–70° at 25 mm. is redistilled and yields 36 g. (75% yield) of a colorless oil boiling at 172° at 28 mm., n_D^{30} 1.529, D_{25}^{30} 1.258.

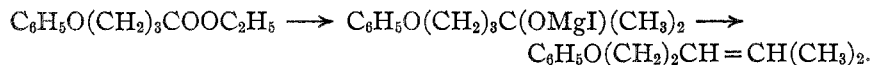
Subs., 0.2766; AgBr, 0.2093.

Calc. for C₁₁H₁₅OBr: Br, 32.9. Found: 32.2.

Phenoxy-5-pentene-2, C₆H₅OCH₂CH₂CH=CHCH₃.—A mixture of 30 g. of phenoxy-5-bromo-2-pentane and 200 cc. of a 10% alcoholic potassium hydroxide solution is refluxed for 10 hours. At the end of this time the mixture is poured into water, the oil separated and taken up in ether. The ether is dried, distilled and the residue fractionated under diminished pressure. The crude fraction from 122–130° at 25 mm. on redistillation gives 14 g. (70% yield) of a colorless oil boiling 132° at 32 mm., n_D^{30} 1.5005, D_{25}^{25} 0.957. At ordinary pressures the substance boils at 226°.

Twenty g. of this ether was heated to boiling for 12 hours. The boiling point remained absolutely constant during the whole time and upon distillation at the end of this period showed that no decomposition had taken place.

Phenoxy-5-methyl-2-pentene-2, C₆H₅O(CH₂)₂CH=C(CH₃)₂.—This substance was prepared by the following series of reactions:



Ethyl- γ -phenoxy-butyrate, C₆H₅O(CH₂)₃COOC₂H₅.—The γ -phenoxy-butyric acid was obtained by the acid hydrolysis of β -phenoxy-ethyl malonic ester.¹ A solution of 90 g. (5 moles) of γ -phenoxy-butyric acid in 500 cc. of absolute alcohol is saturated with dry hydrogen chloride and refluxed for 2 hours. Upon cooling, the reaction mixture is diluted with

¹ *Ber.*, 44, 1507 (1911).

water, extracted with ether, the ether solution washed with dil. sodium carbonate solution, then with water and finally dried over sodium sulfate. Upon removal of the ether, the residue is fractionated under diminished pressure and the crude material boiling at 165–180° at 25 mm. fractionated. The pure ester boils at 170–173° at 25 mm., n_D^{33} 1.491, D_{25}^{33} 1.048.

Subs., 0.2834; CO₂, 0.7200; H₂O, 0.1984.

Calc. for C₁₂H₁₆O₈: C, 69.2; H, 7.7. Found: C, 69.3; H, 7.8.

This same ester may be even more conveniently prepared by the action of alcohol and sulfuric acid upon γ -phenoxy-butyronitrile.¹ A mixture of 90 g. of the nitrile, 300 cc. of absolute alcohol, 100 cc. of conc. sulfuric acid is refluxed for 5 hours; upon cooling the mixture is diluted with ice and water and extracted with ether. Upon drying with sodium sulfate, distilling the ether and fractionating the residue under diminished pressure, the ester is obtained with the same boiling point described above.

Phenoxy-5-methyl-2-pentene-2, C₆H₅O(CH₂)₂CH=C(CH₃)₂.—A suspension of 27 g. of magnesium in 400 cc. of dry ether is treated with 160 g. of methyl iodide. The Grignard solution is then added drop by drop to a well-cooled solution of 104 g. of ethyl- γ -phenoxy-butyrate in 300 cc. of dry ether. After all has been added, the mixture is allowed to stand overnight at room temperature. It is then poured on ice, acidified with hydrochloric acid, the ether layer removed, washed with a little sodium hydrogen sulfite to remove traces of iodine, dried over sodium sulfate. After removal of the ether, the residue is fractionated and 2 main portions are obtained, the larger one boiling at 137–8° at 25 mm. and the smaller boiling at 166–167° at 20 mm. This lower fraction is the compound desired. It boils at 241° at 745 mm., n_D^{30} 1.505. The higher boiling fraction was not identified.

Subs., 0.2548; CO₂, 0.7584; H₂O, 0.2114.

Calc. for C₁₂H₁₆O: C, 81.8; H, 9.1. Found: C, 81.2; H, 9.2.

Twenty g. of the ether was refluxed for 12 hours. The temperature remained constant throughout this period and upon distillation at the end there was no indication that any decomposition had taken place.

Phenyl-propargyl Ether, C₆H₅OCH₂C=CH.—This substance has already been prepared by the action of alcoholic potash upon phenyl- β -bromo-allyl ether² and the phenyl- β -bromo-allyl ether has been formed by the action of sodium phenylate upon β -bromo-allyl bromide. In this research, however, it was found that phenyl- β -bromo-allyl ether is much more readily formed by the action of sodium phenylate upon tribromohydrin.

Phenyl- β -bromo-allyl ether, C₆H₅OCH₂CBr=CH₂.—In 300 cc. of absolute alcohol 24 g. of sodium is dissolved and then 94 g. of phenol added

¹ *Ber.*, 24, 2632 (1891).

² *Bull. soc. chim.*, 40, 324 (1883).

to the hot solution. To this mixture 135 g. of tribromohydrin is gradually added. A very vigorous reaction takes place immediately with a copious precipitate of sodium bromide. The alcohol is now distilled off from the water bath, the residue diluted with water, extracted with ether, the ether extract washed with dil. sodium hydroxide solution, and then dried over sodium sulfate. After removal of the ether, the residue is distilled under diminished pressure and the fraction boiling 125–135° at 25 mm. redistilled. It boils practically constant at 135° at 30 mm. and amounts to 84 g. (83% yield).

The formation of the phenyl-propargyl ether from this bromo compound was carried out exactly as described by Henry.¹ When pure, it boils 111–112° at 40 mm. and at atmospheric pressure 209°. The yield is about 53%.

When 20 g. of phenyl-propargyl ether was heated to boiling under a reflux condenser for 5 hours and then allowed to cool, a solid black tar was produced from which no definite substance could be isolated. It was apparent that the ether had completely decomposed. A second experiment was made, refluxing the phenyl-propargyl ether in di-isoamyl ether (b. p. 170°) for 100 hours. Soon after the heating was started, a dark brown solid began to separate out. At the end of the period indicated, the phenyl-propargyl ether was apparently completely decomposed. When the reaction was carried on in exactly the same way but the refluxing continued for 20 hours only, the same tar was obtained but at least $\frac{2}{3}$ of the phenyl-propargyl ether remained unchanged. In none of the experiments was alkali soluble material obtained.

p-Bromophenyl-propargyl Ether, $\text{BrC}_6\text{H}_4\text{OCH}_2\text{C}\equiv\text{CH}$.—This substance was formed by the action of alcoholic potash upon the *p*-bromophenyl- β -bromo-allyl ether which in turn was produced by the action of excess of sodium *p*-bromophenylate upon tribromohydrin.

p-Bromophenyl- β -bromo-allyl ether, $\text{BrC}_6\text{H}_4\text{OCH}_2\text{CBr}=\text{CH}_2$.—The details for the preparation of this substance are the same as those described under the preparation of phenyl- β -bromo-allyl ether. The substance boils at 171° at 22 mm., n_D^{22} 1.587, D_{25}^{22} 1.719.

Subs., 0.3852, 0.2402; AgBr, 0.4928, 0.3054.

Calc. for $\text{C}_9\text{H}_9\text{OBr}_2$: Br, 54.7. Found: 54.1, 54.4.

p-Bromophenyl-propargyl ether, $\text{BrC}_6\text{H}_4\text{OCH}_2\text{C}\equiv\text{CH}$.—The details for the preparation of this ether from the bromo compound just described are just the same as those used in the preparation of the corresponding phenyl ether. The product is obtained in 50% yields, boils at 144° at 24 mm., n_D^{30} 1.567, D_{25}^{30} 1.468.

Subs., 0.3688, 0.3942; AgBr, 0.3377, 0.3609.

Calc. for $\text{C}_9\text{H}_7\text{OBr}$: Br, 38.0. Found: 39.0, 39.0.

¹ *Bull. soc. chim.*, 40, 324 (1883).

Upon refluxing 20 g. of *p*-bromophenyl-propargyl ether, the temperature gradually rose during the course of 30 minutes from 254—266°. Upon cooling the mass set to brittle tar indicating almost complete carbonization. A second experiment was carried out using di-isoamyl ether as a solvent and the solution was heated for 10 hours. Partial decomposition took place but no alkali soluble product was produced.

Phenoxy-acetonitrile, $C_6H_5OCH_2CN$.—This substance has been prepared by the following series of reactions:



The directions described in the literature were followed.¹ The dehydration of the amide, however, was varied so that a better yield could be obtained. The following procedure is very satisfactory.

Phenoxy-acetonitrile, $C_6H_5OCH_2CN$.—75 g. of dry phenoxy-acetamide is placed in a 500 cc. distilling flask and melted. Into this is now poured directly 60 g. of phosphorus pentoxide and the mixture distilled as rapidly as possible. The distillate, containing both nitrile and unchanged amide, is treated with dry ether which dissolves the nitrile but not the amide, so that the latter may be filtered off. Upon distillation of the ether and vacuum distillation of the residue the nitrile is obtained as a colorless oil boiling at 132° at 30 mm. or 235° at 745 mm.

25 g. of phenoxy-acetonitrile upon refluxing 15 hours turned red and finally black, but the temperature remained constant at about 240°. At the end of this time, distillation showed that practically 90% of the material was unchanged.

***p*-Methyl-phenoxy-acetonitrile**, $CH_3C_6H_4OCH_2CN$.—This substance was prepared from *p*-cresol by the same series of reactions used for the preparation of phenoxy-acetonitrile. This method of preparation has not previously been used, but since the details for the various steps are identical with those employed in the same series of reactions using phenol, they are not given here.¹ The *p*-methyl-phenoxy-acetic acid² thus obtained melted at 135°. By esterification the ethyl-*p*-methyl-phenoxy-acetate was formed and proved to be a pleasantly smelling liquid boiling at 266–267° at 740 mm. which is quite different from the constants for this compound as described in the literature.³ It has previously been made from sodium *p*-cresylate and ethyl chloroacetate and the boiling point given was 243° at 752 mm. A sample prepared according to this method gave identically the same boiling point as was obtained by the above method, the esterification of the corresponding acid. The amide⁴ forms

¹ *J. prakt. Chem.*, [2] 20, 275 (1897).

² *Ber.*, 14, 923 (1891).

³ *J. Chem. Soc.*, 103, 1630 (1913).

⁴ *Gazz. chim. ital.*, 22, II, 525 (1892).

from the ester readily by the action of aqueous ammonia at room temperature and the nitrile from the amide by the action of phosphorus pentoxide. The nitrile as obtained was a colorless, pleasantly smelling oil boiling at 148–149° at 28 mm. and upon cooling gave white crystals melting at 40°. These constants correspond to those obtained by Stoermer, for the substance as prepared by the dehydration of *p*-methyl-phenoxy-acetaldoxim.¹

Upon refluxing *p*-methyl-phenoxy-acetonitrile for 24 hours and then allowing to cool, the entire contents of the flask set to a brittle tar, indicating complete decomposition. When refluxed for 15 hours in di-isoamyl ether as a solvent, the larger part of the product proved to be unchanged nitrile; a few grams, however, of a fraction soluble in alkali proved to be *p*-cresol. A repetition of this last reaction but boiling for 90 hours gave practically the same results.

An attempt was made to prepare the *p*-bromo-phenoxy-acetonitrile but it was found impossible to dehydrate the amide without deep-seated decomposition, so that no pure nitrile was obtained. The ethyl-*p*-bromo-phenoxy-acetate was made from an alcoholic solution of sodium *p*-bromophenylate and chloroacetic ester rather than by the bromination of ethyl-phenoxy-acetate as is described in the literature.² The physical constants were the same in both cases. They form white crystals, m. p. 59°.

p-Bromo-phenoxy-acetamide, $\text{BrC}_6\text{H}_4\text{OCH}_2\text{CONH}_2$.—A solution of 130 g. of ethyl-*p*-bromo-phenoxy-acetate in one liter of 80% alcohol is made and then saturated with ammonia gas at 0°. After standing 24 hours a large proportion of the amide crystallizes out in long colorless needles. The solid is filtered off and by concentrating the mother liquors, more amide is obtained. To purify, it is crystallized from dilute alcohol, m. p. 148–9°.

Subs., 0.2850; 17.3 cc. 0.0714 *N* HCl.

Calc. for $\text{C}_8\text{H}_8\text{O}_2\text{NBr}$: N, 6.1. Found: 6.1.

A series of phenyl-benzyl ethers was made by the action of benzyl chloride or bromide, or substituted benzyl chloride or bromide upon phenol or a substituted phenol in the presence of potassium carbonate and acetone as a solvent.

Phenyl-benzyl ether, $\text{C}_6\text{H}_5\text{OCH}_2\text{C}_6\text{H}_5$.—A mixture of 126 g. (one mole) of benzyl chloride, 105 g. (1.1 mole) of phenol, 138 g. of potassium carbonate and 100 cc. of acetone is refluxed for 8 hours. After dilution with water, the benzyl-phenyl ether is taken up in ether, the ether solution washed with aqueous alkali and dried over sodium sulfate. After removing the ether the benzyl-phenyl ether is distilled under diminished pressure. It boils at 178–79° at 35 mm. and melts at 39°.³

Upon refluxing 100 g. of this ether for 4 hours, the temperature of the

¹ *Ber.*, 30, 1700 (1897).

² *J. prakt. Chem.*, [2] 20, 275 (1897).

³ *Ann.*, 217, 43 (1883).

liquid dropped rapidly from 272° to 220°. The contents of the flask was a dark red liquid which was taken up with ether and the ether solution extracted with dil. potassium hydroxide solution. Upon investigation of the alkaline solution it was found that a considerable quantity of phenol was present. The alkali insoluble material contained toluene, unchanged benzyl-phenyl ether and a small amount of a high-boiling product which was not identified.

The following benzyl ethers were also prepared:

	This communication.	In literature.
	M. p.	M. p.
<i>p</i> -Bromophenyl-benzyl ether.....	b ₆₀ 226° 64°	b ₈₀ 226° ⁰¹
<i>p</i> -Nitrobenzyl-phenyl ether.....	91°	91° ⁰²
<i>p</i> -Nitrobenzyl- <i>o</i> -tolyl ether.....	90°	90° ⁰³
<i>p</i> -Nitrobenzyl- <i>p</i> -tolyl ether.....	89°	89° ⁰³
<i>p</i> -Nitrobenzyl- <i>p</i> -methoxy-phenyl ether. Yellow needles from alc.....	88°	
Subs., 0.5352, 26.0 cc. N, 747 mm. and 48°		
Calc. for C ₁₄ H ₁₈ O ₄ N: N, 5.4. Found: 5.4.		
<i>p</i> -Nitrobenzyl- <i>p</i> -bromophenyl ether. Yellow needles from alc.....	112°	
Subs., 0.4416; AgBr, 0.2684.		
Calc. for C ₁₃ H ₁₀ O ₃ NBr: Br, 25.97. Found: 25.86.		
<i>p</i> -Nitrobenzyl-2,4-dibromo-phenyl ether. Yellow needles from alc.....	161°	
Subs., 0.3862; AgBr, 0.3706.		
Calc. for C ₁₃ H ₈ O ₃ NBr ₂ : Br, 41.34. Found: 40.83.		
<i>p</i> -Bromobenzyl- <i>p</i> -bromophenyl ether.....	111°	111° ⁰⁴
<i>p</i> -Bromobenzyl-2,4-dibromo-phenyl ether.....	100°	100° ⁰⁴

The nitro compounds described above when heated to their boiling point gave deep-seated decomposition. Even at lower temperatures, decomposition took place although more slowly. No definite products could be isolated.

The halogenated ethers evolve hydrobromic acid when heated to the boiling point and give in general a certain amount of phenol or substituted phenol and a little toluene or substituted toluene. In every instance complete decomposition took place.

Summary.

1. The preparation of several ethers of each of the following types has been carried out: ROCH=CH₂; ROCH₂CH₂CH=CH₂; ROCH₂C≡CH; ROCH₂CN; ROCH₂R; where R stands for phenyl or substituted phenyl group.

2. A comparison of the stability of these ethers upon heating has been made with the corresponding allyl-phenyl ethers.

¹ *Ann.*, 357, 90 (1907).

² *Ibid.*, 224, 104 (1884); *THIS JOURNAL*, 39, 309 (1917).

³ *Ibid.*, 39, 309 (1917).

⁴ *Ann.*, 357, 90 (1907).

3. It has been found that none of these compounds rearranges into substituted phenols in a manner similar to the allyl-phenyl ethers.

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PROSO MILLET INVESTIGATIONS—ANALYSIS OF THE OIL—A CHARACTERISTIC ALCOHOL.

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While engaged in an exhaustive examination of the grain of the proso millet, with a view to its employment as a commercial food source, certain peculiarities of the ether extract from the finely divided grain came to our attention. These unusual features led to the following series of investigations, which, while as yet open to further work, have brought out several interesting details, when viewed from the standpoint of the cereal analyst.

This variety of millet, termed *proso* from the Russian name for the "true millet," was denominated by Linnaeus, *panicum miliacum*. It is extensively cultivated in the region of the Altai Mountains in Siberia, in Southern Russia, and in the semi-arid areas of eastern and southern Asia, where it constitutes a staple foodstuff for both man and the lower animals. Its botanical name suggests its productivity, which is marked, even in regions where other common grains do not thrive by reason of aridity of climate. Our first undertaking was merely one involving the analysis of the grain to determine its nutritive factors and, particularly, its gluten and gliadin content, as affecting its adaptability as a breadstuff, and so to throw light upon its possibilities as a food crop for our semi-arid regions west of the Missouri River.

The grain upon which we undertook our studies was raised upon the farms of this institution, from specially selected white seed derived by selection from mother seed obtained in Russia by Professor N. E. Hansen, of this college. Two analyses were made upon the seed, the first upon a coarsely ground meal, unbolted, and the second upon bolted flour from the same grade of grain. The former sample consisted of the hulled grain, ground to pass through a 70-mesh sieve but without further treatment. In the second case, the grain, hulled and pulverized, was passed through the ordinary No. 60 mill screen, so producing a flour similar in fineness to the so-called "Red Dog" grade of wheat flour. By this process, the crude fiber content was materially reduced and the percentage of starch was largely increased, as compared with like data from the coarser samples first taken from the unbolted meal. The following table is presented to show in percentages the analytical results from