After standing at 4° most of the material crystallized and formed, upon repeated recrystallization from hexane–ethanol, colorless prisms, m.p. 113–114°.

1′,2′,3′,4′-Tetrahydro-3,4-benzpyrene.—One hundred ninety mg. of substance, 180 mg. of catalyst and 100 ml. of solvent mixture were used. After about 2 hr. of shaking, 2 mols of hydrogen were taken up. The fluorescent solute was then transferred as described into 100 ml. of hexane, adsorbed on the upper 4–5-cm. section of a 28 × 8 cm. column and developed with benzene–hexane 1:3 (the figures on left designate thickness of zones in mm.; "fl." = fluorescence in ultraviolet light):

15 empty section
30 greenish color and fl.: unidentified
15 colorless, blue fl.: mainly unchanged benzpyrene
60 green, purplish fl.: dihydrobenzpyrene, etc.
10 interzone
55 colorless, purplish-blue fl.: tetrahydrobenzpyrene
100 empty section
Filtrate: pale-blue fl.: perhydrobenzpyrene, etc.

The 55-mm. zone was eluted, transferred into hexane, evaporated, dissolved at 60° in the minimum amount of hexane in a conical centrifuge tube, and cooled in ice-water. The crystals were centrifuged, washed with a little cold hexane, centrifuged again and dried *in vacuo;* yield 85 mg. of almost colorless crystals (m.p. 107.5–109.5°) which became colorless upon recrystallization; yield 67 mg. of pure substance, m.p. 111–111.5°. Fieser's synthetic preparation melted at 113–113.5°, and a mixture of the two at 111–112°. Two parallel experiments yielded, respectively, 88 mg. and 88 mg. of end-product and, after recrystallization, 71 and 77 mg. of pure crystals: thin plates with slightly concave sides showing complicated twinning; some four-sided, star-like structures also appeared. The compound is more soluble than 3,4-benzpyrene. Its adsorbates show purplish fluorescence which is markedly less brilliant than that of benzpyrene. For analysis the samples were dried under 1 mm. pressure at 50° for 3 hr.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.96; H, 6.02.

The orange-red trinitrobenzene complex was prepared by combining hot benzene solutions; m.p. 196–197° (after recrystallization from benzene–methanol); under the microscope: short, broad, quadrangular prisms and plates; the color is brownish-yellow, markedly darker than that of the corresponding dihydro derivative; thick individuals are reddish.

Anal. Calcd. for $C_{20}H_{16}$ + $C_6H_5(NO_2)_3$: N, 8.94. Found: N, 9.03.

6,7-Dihydro-3,4-benzpyrene (?).—The 30-, 15- and 60-mm. zones were cut out together, eluted, and transferred into benzene–hexane 1:1. This solution was combined with a similar one obtained in a parallel experiment, and rechromatographed on a 28 × 8 cm. column (developer, benzene–hexane 2:3):

5 green; green fl.: unidentified
40 interzone
45 purple fl.: unchanged 3,4-benzpyrene (34 mg.)
10 interzone
50 dull blue fl.: dihydro-3,4-benzpyrene
15 interzone
65 faint bluish fl.: tetrahydrobenzpyrene (traces)

The dihydro zone was rechromatographed on a 21 × 3.5 cm. column, the main zone eluted, transferred into benzene–hexane 1:1 and evaporated to dryness. The residue was dissolved at 60° in the minimum amount of benzene and crystallized by dropwise addition of cold methanol; yield 32 mg. and, after recrystallization, 22 mg., m.p. 148.5–149°; colorless, long plates with some parallel twinning; the ends of individual crystals are oblique or roof-like. In contrast to benzpyrene, this compound does not show fluorescence in dilutions fit for Beckman readings; at higher concentrations a rather weak bluish fluorescence appears.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.22; H, 5.81.

The spectral curve of the hexane solution showed maxima at 222, 262, 272, 299, 305, 311, 325, 348, 365 mμ and minima at 241, 265, 293, 302, 307, 318, 343, 362 mμ.

When hydrogenated in the presence of PtO_2 the compound added within 24 hr. 9.7 H_2 (calcd. 9.0 H_2).

The 1,3,5-trinitrobenzene complex, obtained by mixing hot benzene solutions, melted sharply at 180–180.5°. Under the microscope thin yellow prisms were observed.

Anal. Calcd. for $C_{20}H_{14}$ + $C_6H_3(NO_2)_3$: N, 8.99. Found: N, 9.29.

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PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Acetylenic Ethers. VI.[1] Phenylalkoxyacetylenes[2]

BY THOMAS L. JACOBS AND WILLARD R. SCOTT, JR.

RECEIVED JULY 31, 1953

Phenylmethoxyacetylene, $C_6H_5C{\equiv}COCH_3$, was synthesized by dehydrohalogenation of bromomethoxystyrene. This acetylenic ether polymerized readily, was easily hydrated in aqueous acid and reacted with methanolic potassium hydroxide yielding phenylacetic acid. Preliminary attempts were made to prepare the corresponding butyl and ethyl acetylenic ethers.

Several acetylenic ethers of the type $HC{\equiv}COR$ have been synthesized by dehydrohalogenation of alkoxyhaloethylenes, $HXC{=}CHOR$[3-9] and in a number of cases the acetylenic hydrogen in the ether has been replaced by an alkyl radical or some other group through the intermediate Grignard reagent, $ROC{\equiv}CMgBr$. No method has been devised for replacing an acetylenic hydrogen by an aryl group, and arylalkoxyacetylenes $ROC{\equiv}CAryl$ cannot be prepared in this way. The only such compound reported in the literature is phenylethoxyacetylene[10] which was believed to result from the action of sodamide in benzene on phenylketene diethyl acetal. This acetylenic ether was not

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[1] For paper V see T. L. Jacobs and W. P. Tuttle, Jr., THIS JOURNAL, **71**, 1313 (1949).

[2] Taken in part from a dissertation presented by Willard R. Scott, Jr., in partial satisfaction of the requirements for the degree Doctor of Philosophy, July, 1950. This work was supported in part by a research contract with the Office of Naval Research.

[3] M. Slimmer, *Ber.*, **36**, 289 (1903).

[4] T. L. Jacobs, R. Cramer and F. T. Weiss, THIS JOURNAL, **62**, 1849 (1940).

[5] T. L. Jacobs, R. Cramer and J. E. Hanson, *ibid.*, **64**, 223 (1942).

[6] A. E. Favorskiĭ and M. N. Shchukina, *Zhur. Obshcheĭ Khim.*, **15**, 385, 394 (1945); *C. A.*, **40**, 4347, 4657 (1946).

[7] D. A. van Dorp, J. F. Arens and O. Stephenson, *Rec. trav. chim.*, **70**, 289 (1951).

[8] M. F. Shostakovskiĭ and F. P. Sidel'kovskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 394, 641 (1950); *C. A.*, **45**, 2851, 8443 (1951).

[9] J. Queck, *Abhandl. brauschweig. wiss. Ges.*, **4**, 37 (1952).

[10] H. Scheibler, E. Marhenkel and R. Nikolic, *Ann.*, **458**, 21 (1927).

isolated in pure condition and the only evidence for its presence mixed with the ketene acetal was the formation of phenylacetic acid by reaction with water. However experiments reported below show that phenylalkoxyacetylenes react less readily with water than phenylketene acetals, which hydrolyze rapidly to alkyl phenylacetates under these conditions.[11,12] Thus there is no evidence that phenylethoxyacetylene was present in the case reported.

It was of interest to prepare arylalkoxyacetylenes for comparison with other acetylenic ethers. This paper describes the synthesis of phenylmethoxyacetylene and a study of its reactions as well as preliminary attempts to prepare phenylethoxyacetylene and phenylbutoxyacetylene.

Phenylmethoxyacetylene (II) was prepared by dehydrobromination of bromomethoxystyrene[13] (I) with powdered potassium hydroxide. Details of this vigorous and erratic reaction are given in the

$$\underset{\text{I}}{C_6H_5CBr{=}CHOCH_3} + KOH \longrightarrow \underset{\text{II}}{C_6H_5C{\equiv}COCH_3} + KBr + H_2O$$

Experimental Part. Except for recovery of starting material, removal of bromine as bromide ion was essentially complete, but the yield of low-boiling, crude product, a mixture of II and methyl phenylacetate, seldom exceeded 20%. Other basic reagents were even less satisfactory. Hot concentrated potassium *t*-butoxide in *t*-butyl alcohol gave a lower yield of acetylenic material. Sodamide in liquid ammonia gave an extremely insoluble polymer. A low yield of a saturated ester was obtained using potassium methylate. Sodium hydroxide, sodium methoxide and sodium hydride gave essentially no reaction with bromomethoxystyrene at temperatures up to 200°.

Separation of the mixture of phenylmethoxyacetylene and methyl phenylacetate by distillation was impossible because the boiling points of the components are very close together at or near 1 mm. and the acetylenic ether polymerizes rapidly when it is distilled at higher pressures. A chemical separation was accomplished by selective saponification of the ester with 0.5 *N* methanolic potassium hydroxide. Although some of the acetylenic ether was destroyed under the mildest conditions which permitted complete removal of the ester, this method was the only one discovered which permitted isolation of pure phenylmethoxyacetylene. The over-all yield based on methoxystyrene was 3%. Attempts to remove methyl phenylacetate from the mixture by reaction with phenylmagnesium bromide or *n*-hexylmagnesium bromide were unsuccessful because the acetylenic ether polymerized during the reaction or during attempts to separate it from the carbinols produced.

Pure phenylmethoxyacetylene was a colorless, pleasant smelling liquid. Hydrogenation over platinum or palladium catalysts resulted in considerable hydrogenolysis to methanol and ethylbenzene. This cleavage may occur directly with the acetylene, or hydrogenation to β-methoxystyrene may be the first step, and the latter may undergo hydrogenolysis. β-Methoxystyrene was found to yield methanol and ethylbenzene about as readily as did phenylmethoxyacetylene, and the relative yields of hydrogenolysis products and methyl β-phenylethyl ether were comparable in the two cases. Hydrogenation of phenylmethoxyacetylene over Raney nickel at room temperature and atmospheric pressure gave no detectable cleavage and methyl β-phenylethyl ether was readily isolated. A rough analysis of the mixtures isolated in the synthetic procedure was realized by such hydrogenation followed by determination of the ester by quantitative saponification.

Hydration of the acetylenic ether occurred readily by boiling with a dilute solution of sulfuric acid in methanol or aqueous methanol; methyl phenylacetate and phenylacetic acid were obtained. Boiling with neutral aqueous dioxane appeared to cause no addition of water, but some polymerization occurred.

The acetylenic ether rapidly absorbed iodine but the product was an unstable liquid which could not be purified. The ether was also sensitive to oxygen but the volume of the gas absorbed by a sample was not large. After standing three days with oxygen the odor of the acetylenic ether could no longer be detected; the product was a yellow, unsaturated liquid which was not examined further.

An outstanding characteristic of phenylmethoxyacetylene is the ease with which it polymerizes. Distillation of the pure compound even at pressures below 1 mm. left a clear, orange glass in 5–10% yield. Inhibitors were unsuccessful in preventing a reaction. The acetylenic ether became colored slowly at 0°; at room temperature about a week was required for essentially complete polymerization. Most polymer samples became partially crystalline on standing or when treated with methanol. The crystalline material was isolated and found to be a trimer. On one occasion a second crystalline product which proved to be a dimer was also isolated. An amorphous residue was also obtained. The trimer would be expected to be 1,3,5-trimethoxy-2,4,6-triphenylbenzene, but degradation experiments were unsuccessful and an attempted synthesis failed; the structure therefore remains uncertain.

In connection with Scheibler's report[10] of the synthesis of phenylethoxyacetylene from phenylketene diethyl acetal by reaction with sodamide, one attempt was made to prepare phenylmethoxyacetylene by dropping phenylketene dimethyl acetal[14] onto powdered sodamide under reduced pressure with continuous distillation of the product; 50% of the starting material was recovered and the remainder of the material was a tar.

The synthesis of phenylethoxyacetylene was attempted from bromoethoxystyrene[13] by the procedure found most successful for the methyl ether. Low boiling material was isolated in somewhat higher yield than attained with the latter; it had a sharp boiling point but proved to be a mixture of

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[11] H. Staudinger and G. Rathsam, *Helv. Chim. Acta*, **5**, 645 (1922).

[12] S. M. McElvain, *Chem. Revs.*, **45**, 453 (1949).

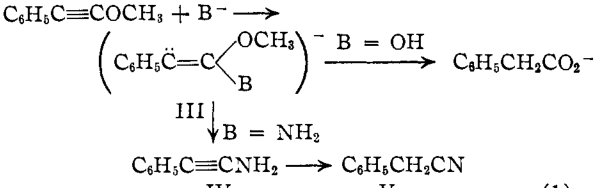
[13] T. L. Jacobs and W. R. Scott, Jr., THIS JOURNAL, **75**, 5500 (1953).

[14] S. M. McElvain and M. J. Curry, *ibid.*, **40**, 3781 (1948).

acetylenic ether and ethyl phenylacetate. Analysis of this mixture by hydrogenation over Raney nickel followed by saponification gave poor results, presumably because some hydrogenolysis of the acetylenic ether occurred. No conditions were found under which the ethyl phenylacetate could be saponified completely without destroying almost all of the ether and further work on this compound was abandoned. Impure phenylethoxyacetylene showed the same ready polymerization observed with the methoxy compound, and as before a crystalline trimer and an amorphous orange residue were isolated.

Preliminary attempts to synthesize phenylbutoxyacetylene from bromobutoxystyrene[13] were made before the best synthesis of phenylmethoxyacetylene had been discovered. Dehydrohalogenation over molten sodium hydroxide–potassium hydroxide eutectic gave a low yield of material with the odor and boiling point expected for acetylenic ether. Analysis indicated that the product was the usual mixture of the desired compound and butyl phenylacetate.

Bromobutoxystyrene was also dehydrohalogenated by treatment with sodamide in liquid ammonia. Benzyl cyanide and butanol were isolated along with a little crystalline polymer which appeared to be a trimer of phenylbutoxyacetylene. The characteristic odor of phenylalkoxyacetylenes was easily detected in this experiment but none of the butyl ether could be isolated. It is not certain that the benzyl cyanide arises from phenylbutoxyacetylene, but it would not be surprising if the acetylenic ether were attacked rapidly by amide ion because methoxide or hydroxide ion attacks phenylmethoxyacetylene readily. This attack by strong bases appears to be characteristic of these ethers (equation 1).



$$C_6H_5C{\equiv}COCH_3 + B^- \longrightarrow \left(C_6H_5\ddot{C}{=}C\begin{matrix}OCH_3\\ B\end{matrix}\right)^- \xrightarrow{B\ =\ OH} C_6H_5CH_2CO_2^-$$

$$\text{III} \downarrow B = NH_2$$

$$\underset{\text{IV}}{C_6H_5C{\equiv}CNH_2} \longrightarrow \underset{\text{V}}{C_6H_5CH_2CN} \qquad (1)$$

IV need not be an intermediate in the formation of V and other paths from III ($B = NH_2$) to V are easily formulated. If IV were formed it would give V because Hofmann degradation of phenylpropiolic amide is known to give V.[15] This reaction will be studied further.

Experimental Part

Phenylmethoxyacetylene (II).—Different samples of bromomethoxystyrene[13] varied in the vigor of their reaction with powdered potassium hydroxide. A few samples reacted so rapidly that the bromoölefin had to be added dropwise to the alkali; and a few reacted so slowly that the usual powdered potassium hydroxide which contained 12 to 15% water had to be replaced with 95% potassium hydroxide. The usual procedure is described below.

A specially constructed, flat-bottomed, Claisen distilling flask, capacity 200 ml., diameter of bottom 9.5 cm., was used for the dehydrobromination. Ground-glass connections were used throughout. A low sidearm led directly downward into a U-shaped receiver cooled in Dry Ice; the far end of this receiver could be connected to a good vacuum pump through auxiliary traps. Access to the reaction flask was through a wide neck which could be closed with a ground-glass stopper.

A layer of 25 g. (0.45 mole) of powdered 85% potassium hydroxide was spread over the bottom of the flask, 25 g. of bromomethoxystyrene (0.15 mole) was poured onto the solid, and the reactants were mixed rapidly. The reaction usually began just as this operation was completed so the stopper was quickly inserted and the initial frothing allowed to proceed for ten seconds under atmospheric pressure. The system was then connected to the pump and the pressure reduced to 5 mm. as rapidly as the reaction would permit. An oil-bath preheated to 130° was raised around the flask as the pressure was being lowered and was maintained at this temperature. After 30 minutes the pressure was reduced to 1 mm. and kept there until distillation ceased.

The product usually weighed about 12 g. of which 3 to 4 g. was water. The organic portion was taken up in ether, dried over potassium carbonate and distilled. At 1 mm., 3 to 4 g. of material, b.p. 50–70°, was obtained. Around 4 g. of starting material was recovered. When the dark, alkaline residue in the special flask was worked up it was possible to isolate 1 g. of neutral material, b.p. 70–90° (1 mm.), 0.5 g. of starting material and 4.5 g. of an unpleasant smelling, acidic oil. A small amount of benzoic acid was isolated from this oil by extraction with hot water. Bromide ion was titrated in the aqueous solution after organic material had been removed, and corresponded to all of the bromine in the bromomethoxystyrene that was not recovered from the reaction mixture. About 80% of the organic matter is accounted for above, and the rest was present as an alkali insoluble, undistillable tar.

The lower boiling distillate was redistilled, b.p. 49–51° (1 mm.). Analyses for carbon, hydrogen and methoxy showed that a mixture was on hand and suggested that methyl phenylacetate was the impurity. Hydrogenation of this material over Raney nickel at room temperature and atmospheric pressure followed by saponification by heating for 30 minutes in 0.5 *N* methanolic potassium hydroxide and determination of ester present by titration of the basic solution indicated that the sample was 70–80% acetylenic ether and 30–20% methyl phenylacetate. Methyl β-phenylethyl ether and phenylacetic acid were recovered from the reaction mixture. The sum of the weights of phenylmethoxyacetylene indicated by hydrogenation and methyl phenylacetate indicated by saponification was 95–99% of the weight of sample taken. A sample which showed 30% ester in the above procedure gave 40% ester when saponified for 15 minutes without hydrogenation and 62% after 30 minutes of heating. When platinum or palladium catalysts were used for the hydrogenation in the above analysis, total values of 120% or above were recorded because hydrogenolysis occurred.

To isolate pure phenylmethoxyacetylene, 11 g. of low boiling material (from several dehydrohalogenations) was refluxed for 20 minutes with 100 ml. of 0.5 *N* methanolic potassium hydroxide, the reaction mixture cooled, poured into 200 g. of water and ice, and extracted with four 100-ml. portions of petroleum ether (b.p. 30–50°). The extract was dried over sodium sulfate and then shaken with powdered potassium hydroxide, the solvent was removed at reduced pressure below 10° through a small column and the residue distilled rapidly at 1 mm. from a small Claisen flask with low sidearm, yield 5.7 g., b.p. 55–65°. Redistillation gave pure phenylmethoxyacetylene, b.p. 55–58° (1 mm.), $n^{25}{}_D$ 1.5481, $d^{25}{}_4$ 1.0149, *MR*D calcd. 39.81, *MR*D obsd. 41.38.

Anal. Calcd. for C_9H_8O: C, 81.79; H, 6.10; OCH_3, 23.48. Found: C, 81.73; H, 6.15; OCH_3, 23.35.

Polymers of Phenylmethoxyacetylene.—Whenever samples containing phenylmethoxyacetylene were distilled at 1 mm. there remained in the distilling flask a clear, viscous orange resin amounting to 5–10% of the acetylenic ether originally present. On standing for some time crystals usually appeared in this glass or the crystallization could often be hastened by dissolving the resin in ether and precipitating with methanol. After no more crystalline material could be obtained by the ether–methanol treatment, removal of the solvents left a red gum. A brown amorphous powder was obtained from this by precipitation from ether by addition of petroleum ether. Removal of solvents from the filtrate left a dark red, glassy resin. These amorphous materials were not examined further.

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(15) I. J. Rinkes, *Rec. trav. chim.*, **39**, 704 (1920).

Except for one instance the crystalline material was a single, white compound which was purified by recrystallization from methanol and from petroleum ether, m.p. 165–166°.

Anal. Calcd. for $(C_9H_8O)_3$: C, 81.79; H, 6.10; OCH_3, 23.48; mol. wt., 396.5. Found: C, 82.40; H, 6.47; OCH_3, 23.4; mol. wt. (Rast), 360.

On one occasion after the first crop of crystals had been separated as usual, evaporation of the methanol gave a new material which was purified by recrystallization from methanol, m.p. 134–135°.

Anal. Calcd. for $(C_9H_8O)_2$: C, 81.79; H, 6.10; mol. wt., 264.3. Found: C, 81.64; H, 5.79; mol. wt. (Rast), 240.

Phenylethoxyacetylene.—Using the directions for phenylmethoxyacetylene, 25- to 30-g. samples of bromoethoxystyrene[13] were treated with powdered potassium hydroxide to give 30–35% yields of crude material, b.p. 60–70° (1 mm.). Analysis of this distillate by hydrogenation over Raney nickel and quantitative saponification of the saturated solution gave 93–96% acetylenic ether and 24–25% ester (total 117–121%) which suggests that hydrogenolysis occurred even under these mild conditions. Purification of the acetylenic ether was attempted as for the methyl ether; a 5.5-g. sample was isolated, b.p. 49–50° (0.5 mm.), $n^{25}D$ 1.5421.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90; for $C_{10}H_{12}O_2$ (ethyl phenylacetate): C, 73.15; H, 7.36. Found: C, 80.64; H, 7.79.

Analysis of this purified sample as above showed 11% ester; the hydrogen uptake corresponded to 100% acetylenic ether.

The residues from the distillation or from allowing the impure phenylethoxyacetylene to stand closely resembled those from phenylmethoxyacetylene. White crystals were isolated, m.p. 170–170.5°, from methanol.

Anal. Calcd. for $(C_{10}H_{10}O)_3$: C, 82.16; H, 6.90; mol. wt., 438.5. Found: C, 82.03; H, 6.95; mol. wt. (Rast), 430.

The Reaction of Bromobutoxystyrene with Sodamide.—To 0.1 mole of sodamide[16] in 80 ml. of liquid ammonia was added dropwise with stirring 9.5 g. (0.037 mole) of bromobutoxystyrene.[13] After 15 minutes of stirring, 5 g. of ammonium nitrate and then 50 ml. of water were added (slowly at first). The reaction mixture was extracted with ether, the ether solution dried over anhydrous potassium carbonate, filtered, and the ether removed under reduced pressure. The red oil which remained was distilled from a Claisen flask into a receiver cooled in Dry Ice. Redistillation through a small column gave 1.6 g., b.p. 100° (12 mm.), $n^{25}D$ 1.5210. Known benzyl cyanide gave the same b.p. through the column and the same refractive index.

Anal. Calcd. for C_8H_7N: C, 82.02; H, 6.02. Found: C, 82.15; H, 5.95.

Hydrolysis with sulfuric acid gave phenylacetic acid in 86% yield, m.p. crude 74–76°.

The Dry Ice trap in the distillation yielded a little butyl alcohol identified as its phenylurethan, m.p. and mixed m.p. 61–62°.

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[16] T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Bromoalkoxystyrenes[1]

BY THOMAS L. JACOBS AND WILLARD R. SCOTT, JR.

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Dehydrobromination of alkoxystyrene dibromides by several methods gave bromoalkoxystyrenes. These were shown to have the structure $C_6H_5CBr{=}CHOR$, but small amounts of the isomeric compounds, $C_6H_5CH{=}CBrOR$, were also present. These structures were established by acid hydrolysis and ozonization. Methoxystyrene dibromide was also converted to α-bromophenylacetaldehyde and to the corresponding acetal.

Haloalkoxystyrenes of the type $C_6H_5CX{=}CHOR$ or $C_6H_5CH{=}CXOR$ were needed for the synthesis of acetylenic ethers.[2] Compounds of the first sort were unknown when the present investigation began, but a brief report of the preparation of α-bromo-β-methoxystyrene by distillation of α-bromophenylacetaldehyde dimethyl acetal has since appeared.[3] The formation of β-chloro-β-ethoxystyrene, a compound of the second type, by the action of alcoholic potassium hydroxide on chlorophenylacetylene also has been reported.[4] The only product obtained from bromophenylacetylene under the same conditions was phenylacetic acid.[4,5]

The synthetic method investigated in the present work is summarized in equation 1. It was chosen because the starting materials are readily available and the first two steps proceed easily in excellent yield. Removal of hydrogen bromide from II to yield bromoalkoxystyrenes was attempted by several methods, but no completely satisfactory procedure was found. The products, which had the expected composition but broad boiling points, could have been mixtures of four different compounds: *cis-* and *trans-*α-bromo-β-alkoxystyrenes (III) and β-bromo-β-alkoxystyrenes (IV). Evidence was obtained which indicated that compounds of structure III were the principal components, but compounds of structure IV were also present in some of the products. It would be desirable to obtain a pure stereoisomer of structure III in which the hydrogen and bromide atoms were *trans* because this should yield the acetylenic ether readily, but no progress has yet been made toward a stereospecific synthesis or the separation of the isomers.

$$\begin{array}{l} C_6H_5C{\equiv}CH + ROH \xrightarrow{NaOR} \\ \qquad \underset{\text{I}}{C_6H_5CH{=}CHOR} \xrightarrow{Br_2} \underset{\text{II}}{C_6H_5CHBrCHBrOR} \\ \longrightarrow \underset{\text{III}}{C_6H_5CBr{=}CHOR} \text{ or } \underset{\text{IV}}{C_6H_5CH{=}CBrOR} \quad (1) \end{array}$$

Alkoxystyrenes I were prepared with R = methyl, ethyl and butyl. All were converted to bromoalkoxystyrenes, but most of the work was done on the methoxy compound. The best results in the dehydrohalogenation of dibromide

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[1] Taken in part from a dissertation presented by Willard R. Scott, Jr., in partial satisfaction of the requirements for the degree Doctor of Philosophy, July, 1950.

[2] T. L. Jacobs and W. R. Scott, Jr., THIS JOURNAL, **75**, 5497 (1953).

[3] S. M. McElvain and M. J. Curry, *ibid.*, **70**, 3781 (1948).

[4] J. U. Nef, *Ann.*, **308**, 264 (1899).

[5] V. Grignard and H. Perrichon, *Ann. chim.*, [10] **5**, 5 (1926).