solved in concentrated sulfuric acid at room temperature. A momentary flash of bright yellow was produced and on pouring the solution into water a high yield of pure tetraphenylethylene was obtained.

Summary

1. In contrast to unsubstituted neopentyl systems, α-phenylneopentyl systems react with electrophilic reagents to yield largely unrearranged products. α-Phenylneopentyl alcohol with hydrogen bromide yields largely the corresponding bromide, and the latter with silver nitrate regenerates mainly the original alcohol.

2. Asymmetrical tetraphenylethyl alcohol with hydrogen bromide or concentrated sulfuric acid at room temperature yields tetraphenyl ethylene.

3. The effect of substituents on the tendency to rearrangement of neopentyl systems is discussed.

Acetylenic Ethers. III.[1] Halogen Derivatives of Phenoxyacetylene

BY THOMAS L. JACOBS AND WENDELL J. WHITCHER[2]

At the outset of our study of acetylenic ethers it seemed possible that these compounds would exhibit many of the peculiarities of halogenated acetylenes since in both classes the carbon–carbon triple bond is directly attached to an atom bearing unshared pairs of electrons. Actually very few close similarities have been observed. The only one worthy of mention is the great tendency toward polymerization exhibited in both series by those members which have an acetylenic hydrogen (HC≡COR and HC≡CX); compounds in which this hydrogen is replaced by an alkyl group are relatively stable. Dihalogenated acetylenes, XC≡CX, are likewise characterized by ready polymerization. The preparation of halogenated phenoxyacetylenes, $C_6H_5OC≡CX$, was therefore undertaken in order to compare these two series more closely and to examine further the reactions of acetylenic ethers. Since phenoxyacetylene was the most readily available of these ethers it was used throughout this investigation.

Three general methods have been used for the preparation of halogenated acetylenes: the action of halogens or certain halogenating agents on metallic derivatives of acetylenes, the reaction between hypohalite ion and acetylenes, and the treatment of dihaloethylenes with alkaline reagents.

Iodoacetylenes have been prepared in excellent yield by the action of iodine on acetylenic Grignard reagents; at 0° neither diacetylene formation nor iodine addition occurred.[3] Sodium, copper and silver acetylides have also been used and the iodination of the first of these in liquid ammonia is a good synthetic method.[4] Diiodoacetylene has been prepared in excellent yield by passing acetylene into potassium hydroxide solution while iodine in potassium iodide solution was being added.[5] This reaction has not been applied to the synthesis of substituted iodoacetylenes.

All of these methods were tried unsuccessfully in an attempt to prepare iodophenoxyacetylene. The reaction of phenoxyethynylmagnesium bromide with the theoretical amount of iodine at 0° failed to give this compound. Phenoxytriiodoethylene was obtained in fair yield and was the only product isolated. Sodium phenoxyacetylide was similarly treated with iodine and only a small amount of phenoxytriiodoethylene resulted. The main product polymerized when distillation was attempted at 4 mm. pressure, but at much lower pressures a clear distillate was obtained. This was a mixture containing phenoxyacetylene and unstable iodo compounds. Treatment with iodine gave only phenoxyacetylene diiodide and no phenoxytriiodoethylene. The distillate darkened rapidly and could not be purified successfully. An attempt to hydrate the undistilled product with mercuric acetate and hydrochloric acid was unsuccessful.
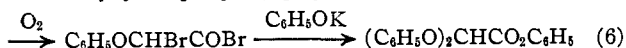
(1) For the second paper of this series see Jacobs, Cramer and Hanson, THIS JOURNAL, 64, 223 (1942).

(2) The greater part of this paper is taken from a thesis presented by Wendell J. Whitcher to the Faculty of Arts and Sciences of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Mr. Whitcher's present address is E. I. du Pont de Nemours and Co., Wilmington, Delaware.

(3) Grignard and Perrichon, Ann. chim., 5, 5 (1926).

(4) Vaughn and Nieuwland, THIS JOURNAL, 55, 2150 (1933).

(5) Biltz and Küppers, Ber., 37, 4412 (1904).

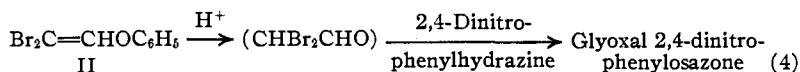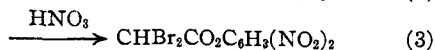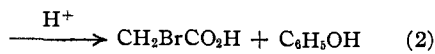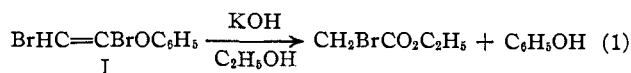Phenoxyacetylene and iodine in potassium iodide solution were added simultaneously to cold potassium hydroxide solution. Phenoxytriiodoethylene was isolated from the reaction mixture by ether extraction and concentration. The residual liquid polymerized when distillation was attempted. The formation of the triiodo compound is accounted for readily only on the assumption that the iodoacetylenic ether is first produced and that iodine is then added.

The synthesis of bromophenoxyacetylene was attempted next in the hope that this compound could be isolated more readily. An early report of its preparation[6] by the action of alcoholic potassium hydroxide on dibromovinyl phenyl ether could not be confirmed by later workers[7,8] who obtained only phenol and ethyl bromoacetate (1).

$$BrHC{=}CBrOC_6H_5 \xrightarrow[C_2H_5OH]{KOH} CH_2BrCO_2C_2H_5 + C_6H_5OH \quad (1)$$

$$\xrightarrow{H^+} CH_2BrCO_2H + C_6H_5OH \quad (2)$$

$$\xrightarrow{HNO_3} CHBr_2CO_2C_6H_3(NO_2)_2 \quad (3)$$

$$Br_2C{=}CHOC_6H_5 \xrightarrow{H^+} (CHBr_2CHO) \xrightarrow[\text{phenylhydrazine}]{2,4\text{-Dinitro-}} \text{Glyoxal 2,4-dinitro-phenylosazone} \quad (4)$$

$$\xrightarrow{KOH} C_6H_5OCH_2CO_2H + \text{polymer} \quad (5)$$

$$\xrightarrow{O_2} C_6H_5OCHBrCOBr \xrightarrow{C_6H_5OK} (C_6H_5O)_2CHCO_2C_6H_5 \quad (6)$$
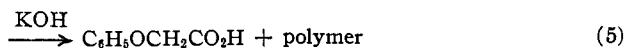
Lawrie tried many alkaline reagents including powdered potassium hydroxide, but was unable to isolate any of the bromoacetylenic ether. All of these workers believed their starting material, prepared by the reaction of tribromoethylene and potassium phenolate, was 2,2-dibromovinyl phenyl ether, II, because it was converted by fuming nitric acid to dinitrophenyl dibromoacetate, (3). Biltz[9] pointed out that the compound was almost certainly 1,2-dibromovinyl phenyl ether, I, since on hydrolysis it yielded a derivative of (mono)bromoacetic acid, (2). He explained the formation during the nitric acid reaction of a compound with both bromines on one carbon as an oxidative rearrangement. It is interesting that Nef's acetylidene theory[8,10] was based largely on structural evidence invalidated by such rearrangements. Since phenoxyacetylene dibromide[11] is identical with the dibromovinyl

phenyl ether described above, it would have been assigned an acetylidene structure, $C_6H_5OCH{=}C$, by Nef. These early workers explained the hydrolytic reactions on the basis of the 2,2-dibromovinyl phenyl ether structure by postulating the intermediate formation of bromophenoxyacetylene and assuming that it added water rapidly

$$Br_2C{=}CHOC_6H_5 \longrightarrow BrC{\equiv}COC_6H_5 \xrightarrow{H_2O} CH_2BrCO_2H + C_6H_5OH$$
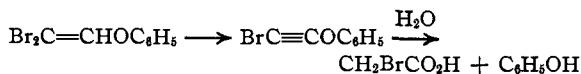
The removal of hydrogen bromide in acid solution to produce a triple bond is of course very unlikely.

Slimmer[7] synthesized a second dibromovinyl phenyl ether by the reactions

$$C_6H_5OCH{=}CHBr + Br_2 \longrightarrow C_6H_5OCHBrCHBr_2 \xrightarrow{KOH} C_6H_5OCH{=}CBr_2$$
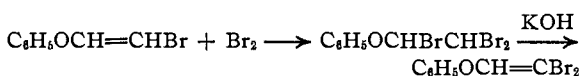
Since the 2,2-dibromo- structure had already been assigned to the compound prepared earlier, he assumed this second one had the 1,2-dibromo- structure. We repeated his synthesis and proved that the compound was 2,2-dibromovinyl phenyl ether, II, by hydrolysis to derivatives of glyoxal, (4).

An attempt to prepare bromophenoxyacetylene from this second dibromo ether by distillation from potassium hydroxide under reduced pressure was not successful. The products were tar and a little phenol and phenoxyacetic acid. The acid was probably formed by hydrolysis of the vinyl ether, but it might also have been produced by hydration of bromophenoxyacetylene, since bromoacetylenes are known to give acids by refluxing with alcoholic potassium hydroxide.[12]

The action of fuming nitric acid at $-10°$ on 2,2-dibromovinyl phenyl ether was very vigorous and the only products isolated were 2,4-dinitrophenol and picric acid. We had no difficulty in confirming the report[8] that under the same conditions 1,2-dibromovinyl phenyl ether underwent a smooth oxidative rearrangement to a dinitrophenyl ester of dibromoacetic acid. It was observed that the 2,2-dibromo compound autoxidized rapidly in the air. It was, therefore, shaken with dry oxygen and the oxidation product treated with potassium phenolate yielding phenyl diphenoxyacetate by an oxidative rearrangement, (6). Foster[13] obtained ethyl diethoxyacetate in a

(6) Sabanejeff and Dworkowitsch, Ann., 216, 279 (1883).
(7) Slimmer, Ber., 36, 289 (1903).
(8) Lawrie, Am. Chem. J., 36, 487 (1906).
(9) Biltz, Ber., 46, 143 (1913).
(10) Nef, Ann., 298, 202 (1897).
(11) Jacobs, Cramer and Weiss, THIS JOURNAL, 62, 1849 (1940).
(12) Nef, Ann., 308, 314 (1899).
(13) Foster, THIS JOURNAL, 31, 596 (1909).

similar manner from 2,2-dichlorovinyl ethyl ether which was prepared by a method that left no question regarding its structure.

Since 1,2-dibromovinyl phenyl ether, m. p. 38–39°, should exist in cis- and trans-forms, an attempt was made to isomerize it by irradiation with ultraviolet light.[14] The product was a liquid from which only a third of the starting material could be recovered. A similar liquid mixture with the composition of dibromovinyl phenyl ether was obtained by adding bromine to phenoxyacetylene.[11] Irradiation of 2,2-dibromovinyl phenyl ether produced no change.

The preparation of bromo- and chloro-acetylenes by the reaction of halogens and acetylenic Grignard reagents is complicated by the ease of addition of the halogen to the triple bond. In view of the isolation of phenoxytriiodoethylene during the addition of iodine to metallic derivatives of phenoxyacetylene, no attempt was made to prepare bromophenoxyacetylene by this method. Since phenoxyacetylene is stable to cold potassium hydroxide its reaction with hypobromite ion in alkaline solution[15] was investigated. Some polymerization of the phenoxyacetylene occurred during the reaction, but the darkening was hardly more than observed with phenoxyacetylene alone. Distillation of the product even at 0° with a mercury vapor pump usually resulted in polymerization to a black, solid mass with evolution of heat. On one occasion this polymerization occurred almost explosively while the distilling flask was standing at 0° at atmospheric pressure. One successful distillation was carried out yielding a substance which darkened rapidly. Addition of bromine to this distillate gave phenoxytribromoethylene and a little phenoxyacetylene dibromide. Undistilled bromophenoxyacetylene gave phenoxytribromoethylene on addition of bromine, and phenyl bromoacetate on hydration.

These experiments show that bromophenoxyacetylene can be prepared, but that purification is very difficult due to polymerization.

Experimental Part

Phenoxytriiodoethylene.—Phenoxyethynylmagnesium bromide[11] from 8.0 g. (0.068 mole) of phenoxyacetylene was cooled to 0° under nitrogen and treated with stirring with 17.2 g. (0.068 mole) of iodine in 150 cc. of ether during two and one-half hours. Stirring was continued for twenty

minutes and the solution was hydrolyzed with cold 5% ammonium chloride solution, washed with water and dried over sodium sulfate. On concentration under reduced pressure a total of 10.3 g. (60% yield) of phenoxytriiodoethylene was deposited in several fractions, m. p. 120–122.5° and 124–126°. These were recrystallized several times from ether and petroleum ether, m. p. 129–129.5°.

Anal. Calcd. for $C_8H_5OI_3$: C, 19.30; H, 1.01; I, 76.48. Found: C, 19.63; H, 1.04; I, 76.66.

Similar addition of iodine to sodium phenoxyacetylide[11] gave phenoxytriiodoethylene in only 1% yield; the main product was an unstable liquid which was distilled using a mercury vapor pump. The distillate was crystalline at −80°, but melted to a colorless liquid at room temperature and rapidly turned green. Analysis showed only 34.28% iodine as compared with 52.00% calculated for iodophenoxyacetylene. The addition of iodine to an ether solution of this liquid gave a little impure phenoxyacetylene diiodide; there was no evidence for phenoxytriiodoethylene which is less soluble than the diiodide and readily separated from it.

The yield of phenoxytriiodoethylene obtained by the simultaneous addition of phenoxyacetylene and iodine in potassium iodide solution to cold potassium hydroxide solution was 28.5%.

2,2-Dibromovinyl phenyl ether was prepared according to Slimmer's direction[7] except that a nitrogen atmosphere was maintained throughout. The product was an oil which was carefully fractionated through a small Podbielniak column packed with a spiral of platinum wire; b. p. 117–118° (6 mm.), $n^{20}D$ 1.6046; yield 48%. This material solidified on standing in the cold; m. p. 29–29.5°. A mixed m. p. with 1,2-dibromovinyl phenyl ether, m. p. 38–39°, showed a depression.

Anal. Calcd. for. $C_8H_6Br_2$: Br, 57.50. Found: Br, 56.89.

Hydrolysis.—Only partial hydrolysis resulted when 1.7 g. (0.006 mole) of 2,2-dibromovinyl phenyl ether was refluxed for four hours with 2.4 g. (0.012 mole) of 2,4-dinitrophenylhydrazine and 20 cc. of concd. hydrochloric acid in 50 cc. of alcohol. A yellow precipitate formed rapidly but even at the end of the reaction the solid present was a mixture with a broad melting point. The odor of unchanged dibromoether was apparent. The reaction mixture was filtered and soluble impurities partly removed from the precipitate by refluxing in ethyl acetate and filtering. The insoluble portion was recrystallized from nitrobenzene giving reddish-orange needles, m. p. 311–312°; Strain[16] reported m. p. 326–328°.

Anal. Calcd. for $C_{14}H_{10}N_8O_8$: C, 40.20; H, 2.41. Found: C, 40.29; H, 2.66.

Autoxidation.—Dry oxygen was passed slowly through 10 g. of 2,2-dibromovinyl phenyl ether with shaking during three days. The product was taken up in 75 cc. of dry benzene and added dropwise to a suspension of 10.5 g. of potassium phenolate in 50 cc. of benzene with cooling. The reaction mixture was stirred and allowed to come to room temperature during two hours and finally refluxed for twenty-five minutes. The benzene solution was washed with water, dried and concentrated. Addition of

(14) These experiments were carried out by Mr. Eugene V. Kleber.

(15) Straus, Kollek and Heyn, *Ber.*, **63**, 1868 (1930).

(16) Strain, THIS JOURNAL, **57** ,758 (1935).

ligroin gave 2.9 g. of phenyl diphenoxyacetate (25% yield). It was recrystallized from benzene and ligroin, m. p. 94.5–95° in good agreement with recorded values.[17]

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.99; H, 5.04. Found: C, 74.81; H, 4.92.

Bromophenoxyacetylene.—A mixture of 0.112 mole of phenoxyacetylene and 200 cc. of 0.56 M potassium hypobromite solution containing potassium hydroxide (2.2 M)[15] was stirred under nitrogen at −5 to −8° for three hours. The product was taken up in ether and the ether solution washed with cold 5% potassium hydroxide and water. After drying over sodium sulfate the ether was partly removed and the solution was transferred to a 25-cc. Claisen flask which had a side arm 2 cm. in diameter bent into a U-shape to serve as a receiver. The flask was partly filled with glass wool to prevent bumping and the remaining ether and unchanged phenoxyacetylene were removed with an oil pump and collected in a trap cooled with acetone and dry-ice. Readmission of air to the flask at this point resulted in polymerization, sometimes almost explosively. Polymerization usually resulted even when distillation was continued without interruption simply by cooling the U-tube side arm in dry-ice and starting the mercury vapor pump. One successful distillation was accomplished yielding 8 g. of a lachrymatory almost colorless substance which was a liquid even at −80°. Small samples rapidly turned green and then black when allowed to warm up to room temperature. Purified carbon tetrachloride was, therefore, added to the remaining material and this solution in an ice-bath was treated dropwise with 3.4 cc. of bromine in carbon tetrachloride. At first, each drop of bromine solution reacted vigorously producing white fumes. The dark solution was washed with water and cold 5% potassium hydroxide. After drying over calcium chloride the carbon tetrachloride was removed under reduced pressure and the product distilled at 2 mm. The first fraction was phenoxyacetylene dibromide (3.65 g.) and the second tribromophenoxyethylene (3.85 g.), m. p. 92–93.5° as shown by a mixed m. p. Polymer accounted for the rest of the starting material.

Bromine in carbon tetrachloride was added similarly to the crude undistilled bromophenoxyacetylene from 14 g. of phenoxyacetylene, yielding 18.5 g. (43%) of phenoxytribromoethylene. There was no evidence of phenoxyacetylene dibromide in this experiment.

A concentrated ether solution of undistilled bromophenoxyacetylene from 7.6 g. of phenoxyacetylene was shaken with a solution of 65 g. of mercuric acetate and 3 cc. of concd. hydrochloric acid in 140 cc. of water at 10°. A greenish, flocculent solid separated, but this redissolved with continued shaking for twenty minutes and intermittent addition of concd. hydrochloric acid (total of 50 cc.). The ether solution was washed with water, dried and the ether removed under reduced pressure. Two distillations of the residue gave 4.2 g. (30% yield) of phenyl bromoacetate. b. p. 140–142° (25 mm.), m. p. 28–28.5°.

Summary

1. Iodophenoxyacetylene could not be obtained by the action of iodine on phenylethynylmagnesium bromide or sodium phenoxyacetylide; triiodophenoxyethylene was the main product in the first case. Phenoxyacetylene and iodine reacted in alkaline solution yielding triiodophenoxyethylene. Liquids which polymerized rapidly were obtained in each instance.

2. The dibromovinyl phenyl ether prepared by Slimmer was shown to be 2,2-dibromo-1-phenoxyethylene. It yielded no bromophenoxyacetylene when distilled from potassium hydroxide.

3. Bromophenoxyacetylene was obtained by the action of potassium hypobromite in alkaline solution on phenoxyacetylene. It polymerized very readily, was successfully distilled only at very low pressures and could not be purified. It was hydrated yielding phenyl bromoacetate; the addition of bromine gave tribromophenoxyethylene.

(17) Scheibler and Depner, *Ber.*, **68**, 2139 (1935).