An equimolecular mixture of *n*-butyllithium and phenylmagnesium bromide gave a positive color test with Michler ketone, but no test with *p*-bromodimethylaniline.

A 25-cc. aliquot of a 75-cc. ether solution containing 0.05 mole of *n*-butyllithium was shaken for one minute with 5 cc. of α-bromonaphthalene and there was obtained, subsequent to carbonation, 2.55 g. (87%) of α-naphthoic acid. To the remainder of the solution was added in one portion 0.05 mole of magnesium iodide in 100 cc. of ether. Vigorous refluxing occurred for a few seconds. After stirring for one and one-half minutes, a 25-cc. aliquot was withdrawn, treated for one minute with 5 cc. of α-bromonaphthalene in 25 cc. of ether and then the mixture was carbonated. No α-naphthoic acid was obtained. A second 25-cc. aliquot, withdrawn after eighty minutes and treated as above, also gave no α-naphthoic acid. The remaining 100 cc. of solution was carbonated by the usual procedure and the yield of valeric acid (by titration) was 76.7%. This result is in good agreement with the 75% yield of valeric acid obtained by the carbonation of *n*-butylmagnesium bromide.[10] Apparently, *n*-butyllithium is converted immediately and quantitatively to the corresponding Grignard reagent upon the addition of an excess of magnesium iodide. The reaction can also be reversed, $RMgX + LiX \rightleftharpoons RLi + MgX_2$, for some unpublished studies by R. N. Meals indicate that some butyllithium is formed from an excess of lithium bromide with *n*-butylmagnesium bromide.

A mixture of 0.04 mole of methylmagnesium iodide in 50 cc. of ether and 0.025 mole of *n*-butyllithium in 30 cc. of ether showed no halogen–metal interconversion with α-bromonaphthalene. Carbonation yielded 55 mg. of an as yet unidentified bromo acid melting between 260–270°, but no α-naphthoic acid.

No halogen–metal interconversion was noted with α-bromonaphthalene with a mixture of 0.08 mole of ethylmagnesium iodide in 50 cc. of ether and 0.05 mole of *n*-butyllithium in 50 cc. of ether.

Acknowledgment.—The authors are grateful to H. B. Willis for assistance.

Summary

Color tests have been proposed for some organolithium compounds. One of these is useful for differentiating organolithium compounds from the corresponding Grignard reagents, to which they are promptly converted by magnesium iodide. The other is useful, with some limitations, for differentiating alkyllithium compounds from aryllithium compounds.

AMES, IOWA RECEIVED MAY 2, 1940

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[10] Gilman and Parker, THIS JOURNAL, **46**, 2816 (1924).

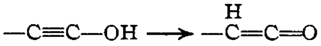
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Acetylenic Ethers. I. Phenoxyacetylenes

BY THOMAS L. JACOBS, RICHARD CRAMER AND F. T. WEISS

Although acetylenic compounds in which the triple-bond carbon is directly attached to oxygen have been mentioned in several places[1] and have been postulated as intermediates in organic reactions as recently as 1937,[2] phenoxyacetylene and benzoylphenoxyacetylene are the only compounds of this type which have been isolated.[3] Phenoxyacetylene was an unstable oil which became a black, viscous mass in a few hours. Its structure was confirmed by analysis and by analyses of the explosive silver and copper derivatives. The substance thought to be benzoylphenoxyacetylene was a stable solid.

Acetylenic ethers are of interest because they are derivatives of an "yne-ol" system related to aldoketenes.



$$—C{\equiv}C—OH \longrightarrow —\overset{H}{C}{=}C{=}O$$

Since such ketene derivatives as ketene acetals[4] are unusually reactive and enol ethers possess an active double bond and are easily hydrolyzed we might expect acetylenic ethers to show considerable reactivity. They might also exhibit some of the peculiarities of halogenated acetylenes.

As a starting point in the study of acetylenic ethers phenoxyacetylene has been obtained by Slimmer's method, its metallic derivatives have been examined and by their use several substituted phenoxyacetylenes in which the acetylenic hydrogen was replaced by alkyl or other groups have been prepared. The parent compound solidifies in dry-ice and can be stored without decomposition at low temperatures. The room tempera-

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[1] (a) Sabanejeff and Dworkowitsch, *Ann.*, **216**, 279 (1883); (b) Nef, *ibid.*, **298**, 337 (1897); (c) Lawrie, *Am. Chem. J.*, **36**, 487 (1906); (d) Grignard and Perrichon, *Ann. chim.*, [10] **5**, 5 (1926); (e) Reihlen, Friedolsheim and Oswald, *Ann.*, **465**, 84 (1928).

[2] Rhinesmith, The action of the Grignard reagent on esters of propiolic acid. A paper presented before the Organic Section of the American Chemical Society at the Rochester meeting, 1937.

[3] Slimmer, *Ber.*, **36**, 289 (1903). The work was done in Nef's laboratory at the University of Chicago.

[4] Beyerstedt and McElvain, THIS JOURNAL, **58**, 529 (1936); **59**, 2266 (1937).

TABLE I

THE REACTIONS OF PHENOXYETHYNYLMAGNESIUM BROMIDE

Reagent	Product	Yield, %[a]	Yield of phenol, %
Ethyl *p*-toluene sulfonate	$C_6H_5—O—C\equiv C—C_2H_5$	15	74
Butyl *p*-toluene sulfonate	$C_6H_5—O—C\equiv C—C_4H_9$	52	38[b]
Acetone	$C_6H_5—O—C\equiv C—C(OH)(CH_3)_2$	63	15
Allyl bromide	Recovered phenoxyacetylene	61	11
Benzoyl chloride	$C_6H_5CO_2C_6H_5$	38	10
Acetaldehyde	$C_6H_5—O—C\equiv C—CH(OH)CH_3$	28[c]	9
Water	$C_6H_5OC\equiv CH$	80	3
Carbon dioxide		0	2
Benzoyl bromide	$C_6H_5CO_2C_6H_5$	26	2

[a] These are yields of carefully purified material. In several instances the reaction indicated was carried out once only. The relative yields either of products or of phenol are not considered as significant. [b] In a second run only 20% of phenol was obtained. [c] The yield of crude methylphenoxyethynylcarbinol was 64% but considerable decomposition and polymerization occurred on fractionation.

ture decomposition is not accompanied by oxygen absorption nor does it seem to be accelerated by light; it is probably a polymerization. A small sample of phenoxyacetylene heated slightly above 100° in a sealed tube exploded violently and left a charcoal-like residue. The structure of phenoxyacetylene was confirmed by catalytic hydrogenation to phenetole, the preparation of a diiodide and dibromide and hydrolysis with concentrated sulfuric acid to phenol, phenolsulfonic acids and acetic acid.

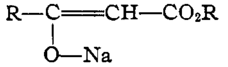
We have repeated the reaction of sodium phenoxyacetylide and benzoyl chloride from which Slimmer reported the isolation in good yield of benzoylphenoxyacetylene and have obtained a product of exactly the same melting point and boiling point as he recorded. Our compound has been shown by analysis and mixed melting point to be phenyl benzoate. In addition we have treated phenoxyethynylmagnesium bromide with both benzoyl chloride and bromide. The principal products were tar and phenyl benzoate. No benzoylphenoxyacetylene was obtained. The ester does not result from heat decomposition of benzoylphenoxyacetylene during distillation since crystallization of the crude product obtained by hydrolysis of the Grignard or sodium acetylide reaction mixture gave only the ester. An attempt was made to prepare acetylphenoxyacetylene from phenoxyethynylmagnesium bromide and either acetyl chloride or acetic anhydride. Much tar resulted, but with acetic anhydride a low yield of phenyl acetate was obtained. Acetylphenoxyacetylene was not isolated.

Phenoxyethynylmagnesium bromide reacted in two ways; in one reaction the metal was replaced as it is in most Grignard reactions, and in the other the two carbon atoms of the acetylenic linkage were lost, the final product being phenol (or phenyl benzoate). A small amount of a brown insoluble material always accompanied the reaction and was probably formed from the acetylenic carbons; very little of this precipitate was produced when phenoxyethynylmagnesium bromide was treated with water or with carbon dioxide. It is clear from Table I that with most reactants the reaction took both courses.

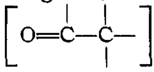
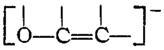
The alkylphenoxyacetylenes are stable liquids which show the usual reactions of the triple bond. Butylphenoxyacetylene gave a liquid dibromide, was readily hydrogenated to hexyl phenyl ether and was stable to sodium ethoxide under conditions which resulted in the complete saponification of phenyl caproate. Hydration of this acetylene with dilute hydrochloric acid in the presence of mercuric acetate gave phenyl caproate. Since phenol and caproic acid do not combine under the conditions of the experiment the ester must result from the addition of water to the triple bond. There was no evidence for the formation of 1-phenoxyhexanone-2 which would have resulted if water had added in the reverse manner to the acetylene. There is thus a marked difference in the behavior of these acetylenic ethers and halogenated acetylenes such as 1-bromoheptyne-1 which yields 1-bromoheptanone-2. It is interesting in this connection that the difference in stability between phenoxyacetylene and alkylphenoxyacetylenes is paralleled by the difference between bromoacetylene and alkylbromoacetylenes.

The production of phenyl benzoate in the reaction of metallic derivatives of phenoxyacetylene with benzoyl halides and the formation of phenol in other reactions of these derivatives are believed to be closely related. The system $C_6H_5OC\equiv C$-

Metal is unique, but does have certain analogies with the metallic derivatives of enols and with Grignard reagents of allylic halides.



$\mathrm{R{-}\underset{\underset{\displaystyle O{-}Na}{|}}{C}{=}CH{-}CO_2R}$ $\qquad$ $\mathrm{RCH{=}CH{-}CH_2MgBr}$

The reactions of these compounds have been discussed on the basis of mechanisms involving ionization and chelation[5]; if the system is non-ionic it is not certain whether the metallic derivative exists in two forms differing in the position of the metal or a single metallic derivative is capable of reaction so that the entering group may take either of two positions. Young[5] has presented evidence that in the cases of crotyl and methylvinylcarbinyl bromides and cinnamyl chloride the Grignard reagent does exist in two forms. His results were consistent with the belief that no rearrangement occurred when these metallic derivatives were hydrolyzed or underwent a coupling reaction. It is of course not possible to write for $\mathrm{C_6H_5\overset{(2)}{O}{-}C{\equiv}\overset{(1)}{C}{-}MgBr}$ two structures differing in the position of attachment of the metal, nor is it possible to write for the ion $\mathrm{[C_6H_5\underset{(2)}{O}{-}C{\equiv}\underset{(1)}{C}{-}]^-}$ a second form in which the charge resides on the oxygen (2), without cleaving the molecule. However, the system is quite unstable and with many reactants there is a cleavage resulting in separation of the phenoxyl and $\mathrm{{-}C{\equiv}C{-}}$. If the metal-carbon bond is covalent the electron pair must certainly be unequally distributed and the carbon must be relatively negative, as it obviously is in the ionic form. This would leave the electron density high at (1), but due to the polarizability of the triple bond a distribution of the effect over the system would take place and could, under the influence of the various reactants, result in a high electron density at (2) followed by loss of phenoxide ion or a reaction in which the phenoxyl becomes incorporated in another molecule (formation of phenyl benzoate). According to this idea, which is not new, reactions occur when the electron density becomes critically high and the different results with different reactants can be explained by this polarizing influence. The same picture may account for the different amounts of "normal" and "abnormal" products obtained by using different carbonyl compounds with any given allylic Grignard reagent. Since the properties of resonating systems are believed to be due not to a statistical average of the two or more resonating forms, but to a single molecular structure[6] which may react in either form depending upon the contribution of each and upon other factors such as conditions and reagents, it is believed that the enolate ion,  $\left[\mathrm{O{=}\overset{|}{C}{-}\underset{|}{\overset{|}{C}}{-}}\right]^-$ and  $\left[\mathrm{\overset{|}{O}{-}\overset{|}{C}{=}\overset{|}{C}{-}}\right]^-$, fits into the same picture.

It seems certain that the phenoxyl remained attached to the $\mathrm{{-}C{\equiv}C{-}}$ until phenoxyethynylmagnesium bromide entered into reaction, for hydrolysis with water gave a high yield of phenoxyacetylene and very little phenol. Furthermore just one equivalent of methane was produced from phenoxyacetylene by the Zerewitinoff procedure in the Grignard "machine"; no more of the methylmagnesium iodide was used in any cleavage reaction and the gas produced contained no unsaturated hydrocarbons. Phenoxyethynylmagnesium iodide is relatively unstable, however, for when it was prepared in dibutyl ether and heated, phenol was isolated in good yield. A small amount of amorphous material probably accounts for the two carbons of the acetylenic system. This instability is not surprising in view of the reaction of β-halogen ethers with magnesium or sodium to yield ethylene and an alcoholate.[7] We could not induce magnesium to react with bromophenoxyethylene, but cleavage occurred with sodium to yield sodium phenolate and acetylene.

The formation of phenyl benzoate can hardly be the result of a simple metathesis.

$$\mathrm{C_6H_5O{-}C{\equiv}C{-}Na + C_6H_5COCl \longrightarrow C_6H_5CO_2C_6H_5 + Na{-}C{\equiv}C{-}Cl}$$

Although sodium chloroacetylide and chloroethynylmagnesium bromide have not been investigated, metallic derivatives of chloroacetylene with less reactive metals have been isolated.[8] Hydrolysis of the reaction mixtures from benzoyl halides and phenoxyacetylides gave no explosive gas nor was the characteristic odor of chloro- or bromo-acetylene apparent. The black amorphous tar obtained in the reaction was produced during

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[5] Brief reviews and references will be found in Gilman, "Organic Chemistry," John Wiley and Sons, 1938, Vol. I, p. 430; Vol. II, pp. 1636, 1639. Hückel, "Theoretische Grundlagen der organischen Chemie," Akademische Verlagsgesellschaft, Vol. I, pp. 187–189 (1934). The following articles are noteworthy: Adickes, Hessling and Müllenheim, *Ber.*, **66**, 826 (1933); Johnson, THIS JOURNAL, **55**, 3029 (1933); Young, Winstein and Prater, *ibid.*, **58**, 289 (1936); Young, Ballou and Nozaki, *ibid.*, **61**, 12 (1939).

[6] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 408.

[7] Grignard, *Compt. rend.*, **138**, 1048 (1904); Wohl and Berthold, *Ber.*, **43**, 2177 (1910); Tallman, THIS JOURNAL, **56**, 126 (1934).

[8] Wallach, *Ann.*, **203**, 83 (1880); Hofmann and Kirmreuther, *Ber.*, **42**, 4232 (1909).

hydrolysis; it resembled the substance produced when bromoacetylene decomposed spontaneously and contained halogen and a high percentage of carbon. One would expect sodium chloroacetylide to be sufficiently reactive to combine with benzoyl chloride or phenyl benzoate; phenol would be produced from the ester, but very little was found. An attempt to prove the presence of sodium chloroacetylide by the addition of acetone to the reaction mixture before hydrolysis, and isolation of chloroethynyldimethylcarbinol was fruitless.

Experimental

1-Bromo-2-phenoxyethylene.[3]—A solution of 120 g. of potassium phenolate[9] and 200 g. of dibromoethylene[10] in 350 cc. of absolute methyl alcohol was heated in an autoclave so that the temperature reached 90° in six hours and was maintained for twelve hours. The reaction mixture was poured into water and steam distilled. The distillate (2 l.) was diluted with water, the oil separated and the aqueous portion extracted with ether. The combined ether and oil solution was washed with 20% potassium hydroxide to remove phenol completely, once with water, dried over magnesium sulfate and distilled under reduced pressure, b. p. 75–76° (1 mm.), 128–130° (26 mm.); yield 60–80 g. (35–45%). The yield was not affected by longer heating, higher temperature or the substitution of ethyl for methyl alcohol, but was reduced by more rapid heating. The dibromoethylene recovered was entirely the *trans* form, b. p. 106–107°, m. p. −8° to −7°. Van de Walle[10] found that *cis*-dibromoethylene reacted one hundred times faster with alcoholic potassium hydroxide than its isomer. We obtained a slightly lower yield of bromophenoxyethylene from *trans*-dibromoethylene than from the mixture of *cis* and *trans* usually employed. Slimmer[3] obtained 70–80% yields of bromophenoxyethylene in small, sealed-tube runs by allowing the reaction mixture to stand in the cold until all solid dissolved, but we obtained no better than 50% yields by this method. It was uncertain from his directions whether four-fifths or 4 to 5 molar amounts of potassium phenolate were used, but a run using 4 moles of phenolate to 1 of dibromoethylene gave a 9% yield of material with the composition of diphenoxyethylene, b. p. 102–103° (1 mm.), and a mixture of products boiling 62–80° (1 mm.). One of these was bromophenoxyethylene and the other had the composition of a dibromophenoxyethylene.

Anal. Calcd. for $C_8H_6OBr_2$: C, 34.57; H, 2.18. Found: C, 34.68, 34.50; H, 2.34, 2.09.

Bromophenoxyethylene was fractionated before use, b. p. 99–100° (8 mm.), $n^{20}{}_D$ 1.5759.

Anal. Calcd. for C_8H_7OBr: C, 48.28; H, 3.54. Found: C, 48.56; H, 3.36.

Phenoxyacetylene.—A mixture of 80 g. of powdered potassium hydroxide and 35 g. of bromophenoxyethylene in a 250-cc. Claisen flask was heated fairly rapidly at 23–25 mm. in an oil-bath. A vigorous reaction occurred when the oil-bath was about 100° and the product distilled very rapidly. The phenoxyacetylene solidified in the receiver, which was a U-tube cooled in dry-ice, and was less colored if a small condenser was placed on the side arm as close as possible to the flask. By further reducing the pressure and raising the temperature, a little bromophenoxyethylene could be recovered, but no more phenoxyacetylene. The flask residue contained about 1.7 g. (12%) of phenol. The crude phenoxyacetylene was dried in ether over sodium sulfate at 0° for one or two hours and redistilled with the receiver in dry-ice. The yield was 13–15 g. (60–80%), b. p. 62–63° (25 mm.); 43–44° (10 mm.); m. p. −37 to −36°; $n^{20}{}_D$ 1.5125; $d^{20}{}_4$ 1.0164; MR_D obsd. 34.9; calcd. 35.12.[11] The pure product, a white solid, turned pink on melting and darkened fairly rapidly at room temperature unless kept in ether solution. A sample left at 30° for forty-eight hours was a dark red, viscous mass, but 75% of the phenoxyacetylene could be recovered by dissolving in ether, washing with 10% potassium hydroxide and water, drying and distilling as before. No phenol was detected among the decomposition products.

Catalytic reduction: using Adams catalyst at atmospheric pressure, 4.85 g. (0.041 mole) of phenoxyacetylene absorbed 1820 cc. (0.081 mole) of hydrogen (standard conditions). Distillation yielded phenetole, b. p. 68–69° (20 mm.), which was identified by conversion into 4-nitro-4′-ethoxybenzophenone,[12] m. p. and mixed m. p. 111–112°.

Phenoxyacetylene dibromide was prepared in carbon tetrachloride and distilled, b. p. 148–150° (31 mm.), 127–128° (12 mm.), 81.5–82° (2 mm.). A redistilled sample which solidified at 0° was analyzed: calcd. for $C_8H_6OBr_2$: C, 34.57; H, 2.18; Br, 57.50. Found: Br, 58.1, 57.6. The product was partly solid at room temperature, and the solid after recrystallization from aqueous alcohol melted at 37–38°. *Anal.* Found: C, 34.88, 34.43; H, 2.55, 2.46. This material has the same m. p. as reported by Slimmer[3] for a dibromophenoxyethylene prepared from tribromoethylene and potassium phenolate and assigned the structure $C_6H_5OCH{=}CBr_2$. It is clear from this work and from other evidence to be reported later that the compound is actually $C_6H_5OCBr{=}CHBr$. The unrecrystallized dibromide is probably a mixture of geometric isomers.

Phenoxyacetylene diiodide was prepared in carbon tetrachloride and recrystallized from alcohol; m. p. 77.5–78.5°. The crystals turned brown in air and liberated iodine when in solution. *Anal.* Calcd. for $C_8H_6OI_2$: I, 68.32. Found: I, 68.56, 68.67.

Phenoxyacetylene was treated with concd. sulfuric acid at 0°. The principal product was a mixture of phenolsulfonic acids which was converted into tribromophenol by shaking with bromine water. The tribromophenol corresponded to an 80% yield of phenol in the hydrolysis. Acetic acid was identified by a Duclaux determination.

A solution of 16 g. of phenoxyacetylene in 50 cc. of ether

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(9) Jones and Cook, This Journal, **38**, 1537 (1916); the phenol content was determined by bromine titration, Redman, Weith and Brock, *J. Ind. Eng. Chem.*, **5**, 389 (1913). This method was used frequently to determine phenol in this work.

(10) Van de Walle, *Bull. soc. chim. Belg.*, **27**, 211 (1913). We used commercial tetrabromoethane from the Dow Chemical Co.

(11) The revised value of 2.336 for $C{\equiv}C$ was used in all calculations of molecular refraction, "Landolt–Börnstein," supp. vol. IIIb, 1695. Other values are taken from "Landolt-Börnstein," 5th ed., Vol. II, 985.

(12) Underwood, Baril and Toone, This Journal, **52**, 4087 (1930).

was washed twice with cold 10% potassium hydroxide and twice with water. After drying and distillation, 13.5 g. (85%) of phenoxyacetylene was recovered. Only 0.06 g. of phenol was found by titration of the alkaline solution.[9]

The Reaction of Sodium Phenoxyacetylide with Benzoyl Chloride.—Sodium phenoxyacetylide was prepared by adding 4.9 g. (0.042 mole) of phenoxyacetylene in 10 cc. of ether to 0.9 g. (0.039 g. atom) of powdered sodium in 25 cc. of ether under nitrogen. The ether boiled gently during the addition, and was refluxed for thirty minutes thereafter, but since the reaction mixture darkened rapidly it was cooled to 0° and treated with 6.6 g. (0.047 mole) of benzoyl chloride (added during fifteen minutes). After forty-five minutes of stirring at room temperature, it was poured into water and the ether solution was washed and dried. Distillation gave 1.5 g. of phenoxyacetylene and 3.6 g. (65%) of phenyl benzoate. The yield of ester was lower when the sodium and phenoxyacetylene were refluxed for several hours; m. p. and mixed m. p. with phenyl benzoate, 68–69°. *Anal.* Calcd. for $C_{13}H_{10}O_2$: C, 78.87; H, 5.09. Calcd. for $C_{15}H_{10}O_2(C_6H_5OC{\equiv}CCOC_6H_5)$: C, 81.06; H, 4.54. Found: C, 78.45; H, 5.49.

Phenoxyethynylmagnesium bromide was prepared under nitrogen in a 3-necked flask provided with mercury-seal stirrer, reflux condenser and dropping funnel by adding the theoretical amount of 2.2 *N* ethylmagnesium bromide to 0.1 mole of phenoxyacetylene in 50 cc. of anhydrous ether with refluxing. The addition and further refluxing occupied three to four hours. The resulting clear, brown solution consisted of two layers which persisted when diluted to several times the initial volume; for most reactions the solution was diluted with an equal volume of ether and the reactant added in ether. After refluxing for several hours the reaction mixture was cooled, treated with water and ammonium chloride solution, separated, washed and dried over sodium sulfate. In some cases the solution was washed with cold 5% potassium hydroxide to remove phenol. When phenoxyethynylmagnesium bromide was treated with sulfonic acid esters, about 10% of the phenoxyacetylene was recovered and this was taken into account in calculating yields.

Attempts were made to purify the insoluble precipitate which was believed to result from the acetylenic carbons in the reaction which produced phenol. This material appeared to be powdery, but filtration left a dark, sticky slime which was partly soluble in acetone. The soluble portion could not be purified. The insoluble substance could be obtained as a brown powder which gave the same qualitative tests as the tar from the reaction of benzoyl bromide and phenoxyethynylmagnesium bromide.

The phenoxyethynylmagnesium bromide from 5.3 g. (0.045 mole) of phenoxyacetylene was treated with wet ether at 0°, then with cold water and ammonium chloride solution, and finally with cold 5% potassium hydroxide. After careful washing with water, drying and distilling 80% of the phenoxyacetylene was recovered. Titration showed 0.13 g. (0.0014 mole) of phenol in the alkaline solution. The phenoxyacetylene recovered was slightly more stable than the starting material.

Butylphenoxyacetylene is a colorless liquid, b. p. 122–123° (14 mm.), 71–72° (1 mm.), n^{20}_D 1.5090, d^{20}_4 0.9551, *MR*D obsd. 54.48, *MR*D calcd. 53.59. *Anal.* Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.70, 82.78; H, 7.81, 7.90.

Ethylphenoxyacetylene.—B. p. 98–99° (20 mm.), n^{20}_D 1.5179, d^{20}_4 0.9823, *MR*D obsd. 45.09, *MR*D calcd. 44.36. *Anal.* Calcd. for $C_{10}H_{10}O$: C, 82.15; H, 6.89. Found: C, 82.46; H, 6.92.

Dimethylphenoxyethynylcarbinol.—Acetone in anhydrous ether was added slowly at 0° to phenoxyethynylmagnesium bromide and the mixture was then refluxed for one and one-fourth hours; b. p. 91–92° (1 mm.), n^{20}_D 1.5220, d^{20}_4 1.0470, *MR*D obsd. 51.33, *MR*D calcd. 50.50. *Anal.* Calcd. for $C_{11}H_{12}O_2$: C, 74.94; H, 6.86. Found: C, 74.59; H, 6.74. Attempts to prepare the *p*-nitrobenzoate using *p*-nitrobenzoyl chloride in pyridine were not successful.

Methylphenoxyethynylcarbinol.—The crude material b. p. 98–103° (1.5 mm.) could not be fractionated without considerable decomposition. Further washing with 10% potassium hydroxide and careful distillation finally gave a pure product, b. p. 88–89° (1 mm.), n^{20}_D 1.5351, d^{20}_4 1.0846, *MR*D obsd. 46.56, *MR*D calcd. 45.88. *Anal.* Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.40; H, 6.06.

This compound and the preceding one were slightly irritating to the skin. They left a clear orange polymer as a flask residue when distilled.

Allyl bromide reacted slowly with phenoxyethynylmagnesium bromide on refluxing for eighteen hours. Phenol and phenoxyacetylene were the products isolated. In a second run which was left standing overnight instead of refluxing the yield of phenol was 9%.

Carbonation of phenoxyethynylmagnesium bromide at 0 to −10° or −30 to −40° gave a rapid reaction and no phenoxyacetylene was recovered. The main product was an oil which could be crystallized from ether at low temperatures, but which soon decomposed to a tar.

Formation of Phenyl Benzoate.—The addition of benzoyl chloride to phenoxyethynylmagnesium bromide was carried out at −15°. The reaction mixture turned dark red immediately and some heat was evolved. After forty-five minutes of stirring at room temperature the cooled solution was treated dropwise with cold water and a black tar was formed. The ether solution was separated, washed and dried. Removal of the ether left a black material which on distillation gave phenyl benzoate. In a second run the crude solid was extracted with hot alcohol. The yield of phenyl benzoate was about the same in both runs.

When a solution of phenoxyethynylmagnesium bromide was added slowly to benzoyl bromide in ether at −10° the behavior of the reaction mixture was the same as described for benzoyl chloride, but the yield of phenyl benzoate was lower. The black insoluble tar was powdered and extracted with ether in a Soxhlet extractor, a little dissolving. The insoluble residue was carefully dried and found to contain about 72% carbon, 5% hydrogen and halogen (nonionic). It behaved like finely divided charcoal when ignited, contained no magnesium and was soluble in cold concd. sulfuric acid.

Hydrogenation of butylphenoxyacetylene at atmospheric pressure using Adams catalyst resulted in the absorption of the theoretical amount of hydrogen. The product from 0.95 g. of the acetylene was distilled, giving 0.75 g. of hexyl phenyl ether, b. p. 130° (22.5 mm.), $n^{20}D$ 1.4950. *n*-Hexyl phenyl ether was prepared by the Williamson synthesis, b. p. 140° (30 mm.), $n^{20}D$ 1.4939. Both samples gave *p*-nitro-*p'*-hexoxybenzophenone,[12] m. p. and mixed m. p. 79–79.5°. *Anal.* Calcd. for $C_{19}H_{21}O_4N$: C, 69.75; H, 6.47. Found: C, 69.98; H, 6.56.

Hydration of Butylphenoxyacetylene.—To 4.96 g. of butylphenoxyacetylene suspended in 10 cc. of water was added with shaking 22 g. of mercuric acetate, 70 cc. of water and 1 cc. of concd. hydrochloric acid in that order. A white precipitate appeared which dissolved as 50 cc. more of concd. hydrochloric acid was added slowly, but a small amount of gum remained; this had dissolved in thirty minutes. The solution was extracted with ether and the ether was washed with sodium bicarbonate solution and dried over sodium sulfate. Distillation gave 2.8 g. of phenyl caproate, b. p. 125–130° (14 mm.), $n^{20}D$ 1.4900. The material was carefully fractionated, b. p. 145° (2.4 mm.), $n^{20}D$ 1.4876, d^{20}_4 0.981. *Neutral equivalent.* Calcd. for phenyl caproate: 192. Found: 194. From 1.1 g. of the ester was obtained 0.6 g. of caproic acid, b. p. 202–204°, by refluxing with alcoholic sodium hydroxide. The anilide was prepared, m. p. and mixed m. p. 96–97°. Phenol was identified as tribromophenol. Phenyl caproate was prepared from caproyl chloride and phenol; b. p. 143° (25 mm.), $n^{20}D$ 1.4853, d^{20}_4 0.987.

Preparation and Pyrolysis of Phenoxyethynylmagnesium Iodide.—When 11.5 g. of phenoxyacetylene in 100 cc. of dibutyl ether was treated with 450 cc. of 0.88 *N* methylmagnesium iodide during two and three-fourths hours at room temperature and then heated at 90–105° for two and one-half hours, the solution was clear yellow and appeared normal. It was cooled to 0° and treated carefully with water and then ammonium chloride solution. The dibutyl ether solution was washed with 10% potassium hydroxide until no more phenol was obtained. Titration indicated 7.84 g. (86%) of phenol. It was possible to isolate 7.5 g. of this in pure condition. The dibutyl ether solution was dried and fractionated under reduced pressure. Besides much dibutyl ether, b. p. 53° (31 mm.), a few tenths of a cc. came over slightly higher and at lower pressure. This had the odor of phenoxyacetylene mixed with dibutyl ether. The flask residue, 0.4 g., was largely tar.

The Action of Sodium and Magnesium on Bromophenoxyethylene.[13]—In a 2-necked, 250-cc. flask provided with a mercury-seal stirrer, dropping funnel, reflux condenser and gas inlet, and arranged so that any gases given off could be swept through the condenser into efficient gas washing bottles was placed 6.9 g. of sodium in 100 cc. of xylene. The sodium was powdered and 19.9 g. of bromophenoxyethylene was added. The material was heated in an oil-bath at 90° with stirring for seventy hours, excess sodium was destroyed with 13 cc. of alcohol after cooling, and all gases were swept through the washing bottles which contained bromine in carbon tetrachloride. The flask contents were then treated with 10% hydrochloric acid, and the ether solution was extracted with 5% potassium hydroxide until no more phenol could be detected. Phenol in the alkaline solution (by titration), 9.23 g. (98.1%). The bromine solution was washed with bisulfite solution and water and distilled under reduced pressure. After removal of the carbon tetrachloride, 7.9 g. of tetrabromoethane (21%) was obtained, b. p. 108° (3 mm.), $n^{20}D$ 1.6349, d^{20}_4 2.9291. Recorded in Beilstein for tetrabromoethane: b. p. 114° (12 mm.), $n^{20}D$ 1.6379, d^{20}_4 2.9638.

The treatment of bromophenoxyethylene with powdered magnesium in dibutyl ether in a similar apparatus, with stirring and heating to 110° for seventy hours, gave no detectable amount of phenol or tetrabromoethane and the magnesium remained unattacked; 85% of the starting material was recovered. The addition of small amounts of a Grignard reagent or iodine did not cause the magnesium to react with the bromo compound.

Summary

1. Phenoxyacetylene has been prepared and its properties studied.

2. Phenoxyethynylmagnesium bromide yields substituted phenoxyacetylenes with various reagents; it fails to react with allyl bromide. Phenol is usually produced in these reactions.

3. Sodium phenoxyacetylide reacts with benzoyl chloride to give phenyl benzoate instead of benzoylphenoxyacetylene as reported by Slimmer. Similar results were obtained from phenoxyethynylmagnesium bromide.

4. The behavior of metallic derivatives of phenoxyacetylene appears to be analogous to that of metallic enolates and allylic Grignard reagents.

5. Butylphenoxyacetylene shows the usual reactions of acetylenes. Water is added in the presence of mercury salts or by refluxing with acid to give phenyl caproate.

LOS ANGELES, CALIFORNIA RECEIVED APRIL 4, 1940

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[13] These experiments were carried out by Mr. Frank C. Wheelock, Jr.