This amine had all the properties of 1-dimethylamino-2,3-diphenylpropane.[7] It formed a methiodide which was hygroscopic. The methochloride formed a chloroplatinate melting at 244–247° dec. and a gold salt melting at 167–169°. The literature[7] reports melting points of 236 and 164°, respectively, for these two compounds.

Pyrolysis of α-Phenylcinnamamidines.—All three N,N-dialkyl-α-phenylcinnamamidines (IV) (2 g.) when distilled at reduced pressure (10–20 mm.) at 180–200° gave α-phenylcinnamonitrile (1.0–1.3 g.).

N-Ethyl-α-phenylcinnamamidine (IVc) distilled practically unchanged at 250–280° under reduced pressure (30 mm.). The hydroiodide (3.5 g.) under similar conditions gave α-phenylcinnamonitrile (1.8 g.).

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Methylphenoxyacetylene and Phenoxypropadiene

BY LEWIS F. HATCH AND HERBERT D. WEISS

RECEIVED OCTOBER 18, 1954

Methylphenoxyacetylene and phenoxypropadiene have been prepared and characterized. The methylphenoxyacetylene was synthesized by the reaction between sodium phenoxyacetylide and methyl iodide. The phenoxypropadiene was prepared by the dehydrobromination of 2-bromo-1-phenoxy-1-propene. Both compounds appear to be stable toward acetylenic–allenic rearrangement under normal preparative and storage conditions.

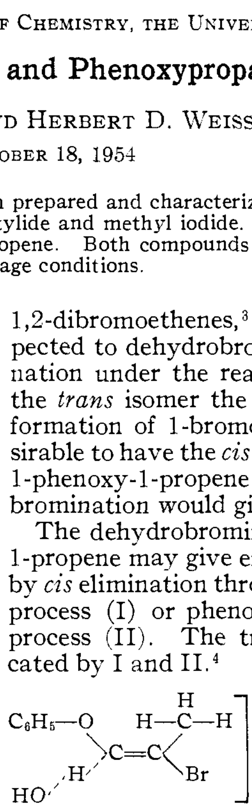
Phenoxyacetylene, ethylphenoxyacetylene and butylphenoxyacetylene have been reported in the literature,[1] but there is no reference to the preparation of either methylphenoxyacetylene or its allenic isomer phenoxypropadiene. Because of the current interest in acetylenic–allenic rearrangements, these two compounds have been prepared.

Methylphenoxyacetylene was formed by the reaction between sodium phenoxyacetylide and methyl iodide in liquid ammonia. The methyl phenoxyacetylene was characterized by its physical properties and molecular refraction (Table I) and by its infrared spectrum (Fig. 1). Its spectrum contains the characteristic —C≡C— stretching frequency at 4.44 μ and does not contain the 5.1 μ absorption characteristic of allenes.[2] The methylphenoxyacetylene apparently does not undergo acetylenic–allenic rearrangement under normal handling conditions, but does decompose quite rapidly at room temperature. Spectral evidence indicated the presence of a phenolic -OH group, probably formed by hydrolysis of the methylphenoxyacetylene. Under rigorously maintained anhydrous conditions, the compound should show a greater stability.

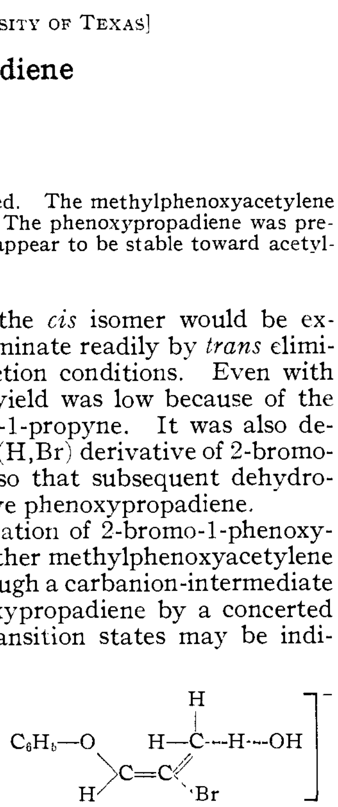
Phenoxypropadiene was prepared by the dehydrobromination of 2-bromo-1-phenoxy-1-propene. This bromide was formed by the reaction between potassium phenoxide and *trans*-1,2-dibromo-1-propene. In this latter reaction it is possible to form either 2-bromo-1-phenoxy-1-propene or 1-bromo-2-phenoxy-1-propene or a mixture of the two. Only one compound was formed, 2-bromo-1-phenoxy-1-propene, and its formation involved the primary bromine atom as would be expected in a reaction between an organic halide and the salt of an organic acid. The absence of the 1-bromo-2-phenoxy-1-propene was confirmed by the fact that the product could be dehydrobrominated.

trans-1,2-Dibromo-1-propene was used instead of either the *cis* isomer or a mixture of the *cis* and *trans* isomers to reduce the side reaction of dehydrobromination to 1-bromo-1-propyne. By analogy to the 1,2-dibromoethenes,[3] the *cis* isomer would be expected to dehydrobrominate readily by *trans* elimination under the reaction conditions. Even with the *trans* isomer the yield was low because of the formation of 1-bromo-1-propyne. It was also desirable to have the *cis*-(H,Br) derivative of 2-bromo-1-phenoxy-1-propene so that subsequent dehydrobromination would give phenoxypropadiene.

The dehydrobromination of 2-bromo-1-phenoxy-1-propene may give either methylphenoxyacetylene by *cis* elimination through a carbanion-intermediate process (I) or phenoxypropadiene by a concerted process (II). The transition states may be indicated by I and II.[4]



I



II

By analogy to the conclusions of Cristol and Norris in respect to the dehydrobromination of *cis*- and *trans*-*p*-nitro-β-bromostyrene[4d] the presence of the aryloxy group on the number 1 carbon atom should favor the dehydrohalogenation by a carbonion-intermediate process by decreasing the negative charge on this carbon atom. The rapid concerted process involving a hydrogen atom of the methyl group still should be the predominant reaction, however.

The phenoxypropadiene was characterized by its physical properties and molecular refraction (Table I) and infrared spectrum (Fig. 1). The spectrum has the 5.12 μ absorption of the allene system and does not contain an absorption characteristic of an acetylene.

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

[2] T. L. Jacobs and W. F. Brill, *ibid.*, **75**, 1314 (1953).

[3] H. Van de Walle, *Bull. soc. chim. Belg.*, **27**, 211 (1913).

[4] (a) S. J. Cristol, THIS JOURNAL, **69**, 338 (1947); (b) S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951); (c) S. J. Cristol and A. Begoon, *ibid.*, **74**, 5025 (1952); (d) S. J. Cristol and W. P. Norris, *ibid.*, **76**, 3005 (1954).

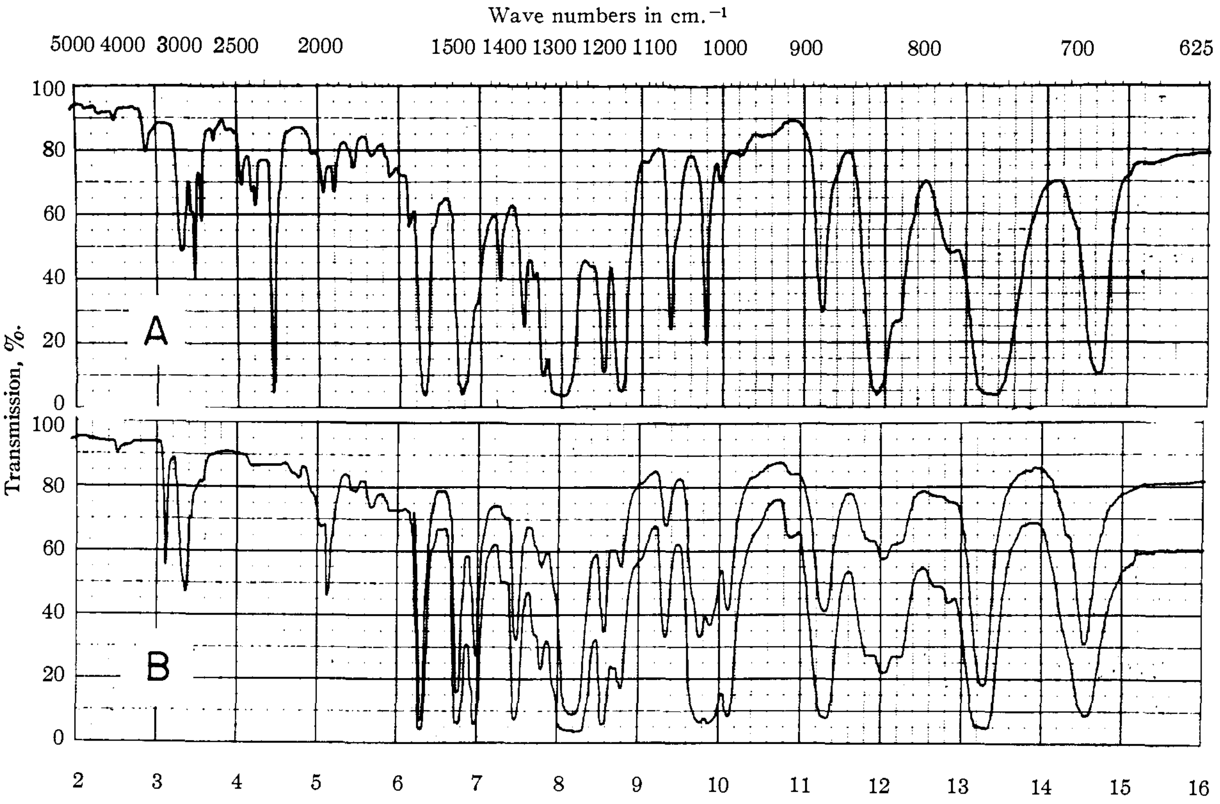

Fig. 1.—Infrared spectra: A, methylphenoxyacetylene; B, phenoxypropadiene.

TABLE I

THE PHYSICAL PROPERTIES OF METHYLPHENOXYACETYLENE AND PHENOXYPROPADIENE

	Methylphenoxyacetylene	Phenoxypropadiene
B.p., °C. (2 mm.)	52.5–53.0	45.5–46.5
n^{20}_D	1.5295	1.5520
n^{25}_D	1.5269	1.5490
n^{30}_D	1.5246	1.5468
d^{20}_4	1.0251	1.0169
d^{25}_4	1.0209	1.0127
d^{30}_4	1.0174	1.0088
*MR*D(obsd.)	39.77	41.30
*MR*D(summation)	39.80	41.48[a]

[a] This figure is based on the value of 3.9 for the allenic (C=C=C) structure as calculated by Jacobs and Brill, THIS JOURNAL, **75**, 1314 (1953).

Experimental

1-Bromo-2-phenoxyethene.—1-Bromo-2-phenoxyethene was prepared by allowing potassium phenoxide to react with dibromoethylene according to the method of Jacobs, Cramer and Weiss.[1] Fractional distillation of the reaction mixture under nitrogen gave 75 g. of unreacted dibromoethylene and 73 g. of 1-bromo-2-phenoxyethene which boiled at 75–76° (1 mm.) and had a refractive index n^{20}_D 1.5753 (lit.[1] b.p. 75–76° (1 mm.), n^{20}_D 1.5759). This represented a 62% conversion and a 52% yield.

Phenoxyacetylene.—Phenoxyacetylene was prepared by the dehydrobromination of 1-bromo-2-phenoxyethene using powdered potassium hydroxide. The powdered potassium hydroxide (80 g.) was preheated to 50° in an oil-bath and 35 g. (0.30 mole) of 1-bromo-2-phenoxyethene was poured into the hot alkali. The remainder of the procedure was similar to that of Jacobs, *et al.* Fractional distillation of the crude phenoxyacetylene gave 17 g. (82.5% yield) of product boiling at 43–44° (10 mm.) which had a refractive index n^{20}_D 1.5125 (lit.[1] b.p. 43–44° (10 mm.), n^{20}_D 1.5125). The phenoxyacetylene was collected with the receiver immersed in Dry Ice. After physical constants and the infrared spectrum were taken the remaining product was stored in anhydrous ether.

Methylphenoxyacetylene.—Methylphenoxyacetylene was prepared by the reaction between sodium phenoxyacetylide and methyl iodide. Sodium phenoxyacetylide was prepared by adding 10 g. (0.085 mole) of phenoxyacetylene in 10 ml. of anhydrous ether to 1.9 g. (0.083 mole) of powdered sodium in 30 ml. of anhydrous ether. The time of addition was 30 minutes, after which time the reaction mixture was maintained at reflux for two hours. Stirring was maintained during the course of the reaction.

A Dry Ice–acetone-bath was placed around the reaction flask and 200 ml. of liquid ammonia was added to the contents of the flask. The contents of the flask were stirred vigorously for one hour and the sodium phenoxyacetylide dissolved in the liquid ammonia during this time. Twenty-three grams (0.16 mole) of methyl iodide in 10 ml. of anhydrous ether was added dropwise to the stirred contents of the flask over a period of 30 minutes. Stirring was continued for 14 hours, after which time the Dry Ice–acetone-bath was removed and half the liquid ammonia was allowed to evaporate. One hundred milliliters of concentrated ammonium hydroxide was added dropwise to the reaction mixture and then 50 ml. of water was added cautiously.

The organic layer was separated and the water layer was washed with two 10-ml. portions of ether. The organic layers were combined, washed with 10% sodium bicarbonate solution, with water and then dried over sodium sulfate. Fractional distillation under nitrogen gave 3.0 g. of phenoxyacetylene and 5.0 g. of methylphenoxyacetylene boiling at 52.5–53.0° (2 mm.), 67.0–68.0° (10 mm.). This represents a 70% conversion with a 64% yield. The physical constants of methylphenoxyacetylene are in Table I.

The methylphenoxyacetylene was collected and stored at Dry Ice temperature. At room temperature it rapidly decomposed.

Anal. Calcd. for C_9H_8O: C, 81.79; H, 6.11. Found: C, 82.28; H, 6.28.

2-Bromo-1-phenoxy-1-propene.—2-Bromo-1-phenoxy-1-propene was prepared by the reaction between potassium phenoxide and *trans*-1,2-dibromo-1-propene. A mixture of the *cis* and *trans* isomers of 1,2-dibromo-1-propene (from Columbia Organic Chemicals) was distilled through a three-foot, glass-helix packed column at 28 mm. The fraction boiling at 38.0–39.5° was collected as the *trans* isomer, lit.[5] b.p. 40.9° (28 mm.).

One hundred twenty grams (0.91 mole) of potassium phenoxide in 350 ml. of methanol and 214 g. (1.15 moles) of *trans*-1,2-dibromo-1-propene were placed in a glass container in a 2-liter stainless steel pressure reactor. The reactor and its contents were heated to 95° over a period of six hours. This temperature was maintained for 24 hours, after which time the reactor was allowed to cool to room temperature overnight.

The reactor was opened cautiously because of the possibility of the formation of flammable 1-bromo-1-propyne[6] from the dehydrobromination of the *trans*-1,2-dibromo-1-propene. Apparently an appreciable quantity was formed. The reaction mixture was steam distilled. A colorless oil was separated and the water layer was continuously extracted with ether for 24 hours. The organic layers were combined, washed with 20% potassium hydroxide solution to remove the phenol, with water, and then placed over magnesium sulfate.

Fractional distillation under nitrogen gave 107 g. of *trans*-1,2-dibromo-1-propene and 9.0 g. of 2-bromo-1-phenoxy-1-propene boiling at 72.5–73.0° (1 mm.). This represents a 50% conversion with a 7.5% yield. A center cut of this product had the following physical constants: b.p. 72.5–73.0° (1 mm.), n^{20}_D 1.5556, n^{25}_D 1.5540, n^{30}_D 1.5521; d^{20}_4 1.3871, d^{25}_4 1.3821, d^{30}_4 1.3771; MR_D obsd. 49.10, MR_D calcd. 49.35.

Anal. Calcd. for C_9H_9OBr: Br, 38.97. Found: Br, 38.83, 38.91.

Phenoxypropadiene.—Phenoxypropadiene was prepared by the dehydrobromination of 2-bromo-1-phenoxy-1-propene using powdered potassium hydroxide. Forty grams (0.71 mole) of powdered potassium hydroxide was placed in a 125-ml. Claisen flask and heated to 50° in an oil-bath. Eighteen grams (0.085 mole) of 2-bromo-1-phenoxy-1-propene was added to the hot alkali, the pressure lowered to 17 mm., the flask heated rapidly. A vigorous reaction occurred at 90° and the product distilled over rapidly. The product was collected in a receiver immersed in Dry Ice. The crude phenoxypropadiene was dried in ether over sodium sulfate. Fractional distillation under nitrogen gave 5.5 g. (50% yield) of phenoxypropadiene boiling at 45.5–46.5° (2 mm.). The physical constants are in Table I.

Anal. Calcd. for C_9H_8O: C, 81.79; H, 6.11. Found: C, 81.39; H, 5.91.

Infrared Spectra.—The infrared spectra of 2-bromo-1-phenoxy-1-propene, methylphenoxyacetylene and phenoxypropadiene were obtained through the courtesy of William F. Hamner and the Monsanto Chemical Co., Texas City, Texas. A Baird Associates double-beam recording infrared spectrophotometer equipped with sodium chloride optics was used. The cell thickness was 0.025 mm. The infrared spectra of methylphenoxyacetylene and phenoxypropadiene are given in Fig. 1.

The following are the principal wave lengths in microns for 2-bromo-1-phenoxy-1-propene (w = weak, vw = very weak, m = medium, s = strong, vs = very strong): 3.31 m, 3.51 w, 5.20 vw, 6.12 m, 6.28 s, 6.73 s, 6.92 w, 7.28 m, 7.92 w, 8.24 vs, 8.61 s, 8.78 m, 9.32 m, 9.61 s, 9.80 w, 10.1 vw, 10.39 w, 10.95 s, 11.20 m, 12.05 w, 12.78 w, 13.27 s, 14.56 m.

Austin 12, Texas

(5) H. A. Smith and L. E. Line, This Journal, **72**, 5434 (1950).

(6) L. F. Hatch and L. E. Kidwell, *ibid.*, **76**, 289 (1954).

[Contribution from the Chemical Laboratories of the University of Maryland]

The Chemistry of 1,3,5-Hexatriene

By G. F. Woods, N. C. Bolgiano and D. E. Duggan

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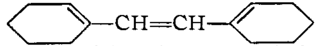
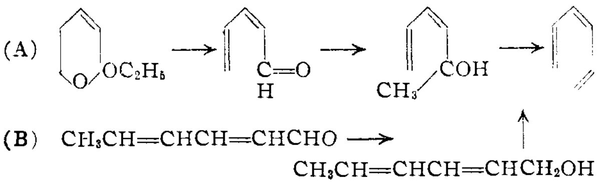
1,3,5-Hexatriene has been obtained by the catalytic dehydration of 2,4-hexadien-1-ol which was prepared by reduction of 2,4-hexadienal with lithium aluminum hydride. Nitrohexatriene was prepared by the nitration of hexatriene. 1,2,3-Benzenetricarboxylic acid was readily synthesized from the Diels–Alder adduct of maleic anhydride and hexatriene. When 1-phenyl-1,3,5-hexatriene was passed over alumina at 350°, it underwent cyclization to yield a phenylcyclohexadiene. This type of cyclization occurs with  which yielded phenanthrene after dehydrogenation; in like manner 2,4-hexadienal and sorbic acid yielded benzene and phenol, respectively.

Earlier syntheses of 1,3,5-hexatriene[1] have involved difficultly available substances. 2,4-Hexadienal,[2] a more convenient starting material, was reduced to the conjugate unsaturated alcohol with lithium aluminum hydride and catalytic dehydration of the alcohol with alumina afforded 1,3,5-hexatriene in excellent yield. The properties of the intermediate, 2,4-hexadien-1-ol, correspond closely with those reported by Reichstein and co-workers.[3] The wide variations reported for the physica constants of 1,3,5-hexatriene[1] could be attributed to either geometrical isomerism or to the identity or purity of the sample. We favor the latter explanation since the same hexatriene is obtained from both 2,4-hexadien-1-ol and 1,3-hexadien-5-ol as



The fact that the same hexatriene is obtained by both A and B indicates that one geometrical isomer is favored; but it is not argued that the *cis* configuration is maintained in A since dehydration over alumina could cause isomerization.

To compare the stability of hexatriene, samples of which have been stored at room temperature with no special precautions and with no discernible polymerization, with that of benzene, nitration of the former was studied. The sulfuric acid–nitric acid method is too drastic, but a 5–10% yield of a nitrohexatriene can be obtained by nitration with acetic acid–nitric acid.

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(1) G. F. Woods and L. H. Schwartzman, This Journal, **70**, 3394 (1948).

(2) Kindly provided by Carbide and Carbon Chemicals Co., New York, N. Y.

(3) T. Reichstein, C. Ammann and G. Trivelli, *Helv. Chim. Acta*, **15**, 264 (1932).