

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of Diarylacetylenes¹

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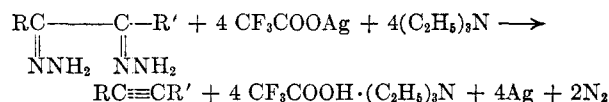
Received November 4, 1957

The synthesis of a number of diarylacetylenes is recorded. A new modification of the Curtius synthesis of diarylacetylenes, involving oxidation of dihydrazones of benzils with silver trifluoroacetate and triethylamine at room temperature, is described.

In this paper are described the syntheses of a number of diarylacetylenes needed for a study of directive effects in hydration of unsymmetrical diarylacetylenes.

p-Chlorophenylphenylacetylene and *o*-chlorophenyl-*p*-chlorophenylacetylene were prepared from 4'-chloro-2-phenylacetophenone and 4'-chloro-2-*o*-chlorophenylacetophenone by treatment with phosphorus pentachloride followed by dehydrochlorination with sodium *t*-butoxide and ethoxide, respectively. However, the attempted dehydrochlorination of the reaction product of 2'-chloro-2-phenylacetophenone and phosphorus pentachloride did not yield a readily purified sample of *o*-chlorophenylphenylacetylene.

This acetylene was made by a new modification of the Curtius method³ since the conventional procedure of heating the dihydrazone of 2-chlorobenzil with yellow mercuric oxide in refluxing benzene did not yield a very pure product. The new modification involves oxidation at room temperature with a solution of silver trifluoroacetate (other silver salts could undoubtedly be used) in triethylamine in acetonitrile or ethanol as solvent according to the following equation:



The course of the oxidation was followed by measuring the nitrogen as evolved. Usually 85–100% of the theoretical nitrogen was obtained in 1–4 hr. The new method was applied to the synthesis of diphenylacetylene, di-*p*-methoxyphenylacetylene, *o*-chlorophenyl-, and *m*-chlorophenylphenylacetylenes in 80–85% yields.

The substituted benzils required for the preparation of the dihydrazones were prepared by oxidation of the corresponding aryl-substituted acetophenones with selenium dioxide⁴ or alternately, and in excellent yield, by oxidation with potassium

permanganate, maintaining a *pH* near 7 by passage of carbon dioxide into the reaction mixture.⁵

All of the isomeric aryl-substituted acetophenones which could result from the hydration of the chlorinated diarylacetylenes were prepared in order that suitable procedures for analysis of the hydration mixtures could be developed. These ketones had all been prepared previously⁶ by the reaction of 3–4 moles of substituted benzylmagnesium halides with appropriate benzamides (40–70 hr. reaction times). We have found that the substitution of benzonitriles for benzamides allows one to use molar amounts of Grignard reagents and a reaction time of 6 hr.

EXPERIMENTAL

Synthesis of chlorinated 2-phenylacetophenones. The crude phenylacetyl chloride, prepared from 114 g. of phenylacetic acid and 160 g. of thionyl chloride in 300 ml. of benzene by refluxing for 10 hr. and removing solvent and excess thionyl chloride under vacuum, was added to a stirred slurry of 134 g. of aluminum chloride in 400 g. of chlorobenzene. The reaction mixture was held at 70° for 90 min., then cooled and poured onto ice to yield 131 g. (68%) of crude solid ketone. After three crystallizations from alcohol colorless plates of pure 4'-chloro-2-phenylacetophenone, m.p. 106.0–107.0°,^{6,7} were obtained.

The remaining ketones were prepared by reaction of *o*-, *m*-, and *p*-chlorobenzylmagnesium bromides with the appropriate benzonitrile. A typical experiment involved addition of 13.8 g. of *p*-chlorobenzonitrile in 100 ml. of ether to a solution prepared by slow addition of 25 g. of *o*-chlorobenzyl bromide in 100 ml. of dry ether to a stirred suspension of 6 g. of magnesium in 150 ml. of ether. After refluxing for 6.5 hr. the mixture was worked up to yield 20 g. (75%) of 4'-chloro-2-(*o*-chlorophenyl)acetophenone, m.p. 103–107. Recrystallizations from alcohol afforded the pure ketone as colorless needles, m.p. 107.4–108.4°. No attempt was made to obtain maximum yields of ketones. The yields of the other crude ketones (melting point of pure ketone in parentheses) were approximately as follows: *p*-chlorobenzylmagnesium bromide on *o*-chlorobenzonitrile, 2'-chloro-2-(*p*-chlorophenyl)acetophenone, 72%, (m.p. 63.0–65.0°); *o*-chlorobenzylmagnesium bromide on benzonitrile, 2-(*o*-chlorophenyl)acetophenone, 55%, (69.0–70.5°); benzylmagnesium chloride on *o*-chlorobenzonitrile, 2'-chloro-2-phenylacetophenone, 71%, (b.p. 144–146° at 1 mm.); benzylmagnesium

(1) Taken from the Ph.D. Thesis of D. E. Reid, The Ohio State University, 1957.

(2) Holder of the Eastman Kodak Co. Fellowship, 1955–1956.

(3) T. Curtius, *Ber.*, **22**, 2161 (1889); T. Curtius and K. Thun, *J. prakt. Chem.*, **44**, 168 (1891).

(4) H. L. Riley, J. F. Morley, and N. A. C. Friend, *J. Chem. Soc.*, 1875 (1932); H. H. Hatt, A. Pilgrim, and W. J. Hurran, *J. Chem. Soc.*, 93 (1936).

(5) Compare to oxidation of stearolic acid, N. A. Khan and M. S. Newman, *J. Org. Chem.*, **17**, 1063 (1952).

(6) S. S. Jenkins, *J. Am. Chem. Soc.*, **55**, 703, 2896 (1933), 56, 682 (1934); S. S. Jenkins and E. M. Richardson, *J. Am. Chem. Soc.*, **55**, 1618, 3874 (1933).

(7) All melting point determinations were taken in a Hershberg apparatus with short range thermometers calibrated by the U. S. Bureau of Standards.

chloride on *m*-chlorobenzonitrile, 3'-chloro-2-phenylacetophenone, 76%, (m.p. 60.4–61.6°); and *m*-chlorobenzylmagnesium bromide on benzonitrile, 2-(*m*-chlorophenyl)acetophenone, 47%, (m.p. 41.8–42.8°).⁸

p-Chlorophenylphenylacetylene. A mixture of 10 g. of 4'-chloro-2-phenylacetophenone and 10 g. of phosphorus pentachloride was heated at 60° for 3 hr. and distilled to yield 8.0 g. of a solid, b.p. 180–185° at 5 mm. This solid was refluxed for 4 hr. in a solution of *t*-butyl alcohol in which 6.7 g. of sodium had been dissolved. About 60% of crude acetylene was obtained which, after several recrystallizations from alcohol, had a m.p. of 81.5–82.0°.

*Anal.*⁹ Calcd. for C₁₄H₉Cl: C, 79.1; H, 4.3; Cl, 16.6. Found: C, 79.1; H, 4.5; Cl, 16.4.

o-Chlorophenyl-*p*-chlorophenylacetylene. A mixture of 5.3 g. of 4'-chloro-2-(*o*-chlorophenyl)acetophenone, 10 g. of phosphorus pentachloride, and 50 ml. of benzene was refluxed for 4 hr. and poured into ice water. The chlorinated products formed were refluxed in a solution of 75 ml. of absolute alcohol in which 3.4 g. of sodium had been dissolved. The crude acetylene thus formed in good but not exactly determined yield was recrystallized twice from aqueous alcohol to yield pure *o*-chlorophenyl-*p*-chlorophenylacetylene, m.p. 62.5–64.5°.

Anal. Calcd. for C₁₄H₈Cl₂: C, 68.0; H, 3.2; Cl, 28.7. Found: C, 67.9; H, 3.3; Cl, 28.5.

o-Chlorophenylphenylacetylene. 2-(*o*-Chlorophenyl)acetophenone (20 g.), selenium dioxide (15.4 g.), and acetic anhydride were heated to reflux for 4 hr. After filtration the reaction mixture was poured into water and the crude *o*-chlorobenzil isolated.¹⁰ Alternatively, this diketone was obtained in similar yield by stirring a solution of 10 g. of ketone, 10 g. of potassium permanganate, 70 ml. of pyridine, and 70 ml. of water at room temperature for seven hours while controlling the pH near 7 by addition of carbon dioxide. By heating the diketone from the former oxidation with 6.4 g. of anhydrous hydrazine and 2 ml. of acetic acid in 250 ml. of alcohol for 18 hr. there was obtained 16.3 g. (69% overall) of colorless dihydrazone. Recrystallization from acetonitrile yielded pure dihydrazone of *o*-chlorobenzil, m.p. 234–236° (dec.).

Anal. Calcd. for C₁₄H₁₃N₂Cl: C, 61.6; H, 4.8; N, 20.5; Cl, 13.0. Found: C, 61.6; H, 5.0; N, 20.4; Cl, 12.8.

(8) All of these ketones have been prepared previously; see reference 6 in this paper.

(9) Analyses by Galbraith Laboratories, Knoxville, Tenn.

(10) E. L. Shapiro and E. L. Becker, *J. Am. Chem. Soc.*, **75**, 4769 (1953).

(11) We thank the General Aniline and Film Corp. for a generous gift of *N*-methylpyrrolidone.

To a stirred solution of 10 g. of dihydrazone in 200 ml. of *N*-methylpyrrolidone¹¹ at room temperature was added 50 g. of silver benzoate in three portions, each followed by the addition of 8 ml. of triethylamine. When the theoretical amount of nitrogen had been evolved (4 hr.) the mixture was filtered, poured into water, and worked up to yield a good but not exactly determined yield of acetylene. A pure 2.5 g. center cut of *o*-chlorophenylphenylacetylene, b.p. 146° at 3 mm. was taken for further work.

Anal. Calcd. for C₁₄H₉Cl: C, 79.1; H, 4.3; Cl, 16.7. Found: C, 78.9, 79.1; H, 4.4, 4.4; Cl, 16.5, 16.4.

m-Chlorophenylphenylacetylene. 3'-Chloro-2-phenylacetophenone was oxidized to *m*-chlorobenzil by the selenium dioxide and potassium permanganate methods described above. A pure sample melted at 88.8–89.8°.¹² The dihydrazone, m.p. 98–99°, was obtained in about 70% over-all yield. The pure dihydrazone, obtained by recrystallization from ethanol-water, melted at 98.4–99.0°.

To a stirred solution of 55 g. of silver trifluoroacetate in 150 ml. of alcohol was added 14.3 g. of *m*-chlorobenzil dihydrazone in 100 ml. of alcohol. During 45 min. five 5-ml. portions of triethylamine were made. After a total of 50 min., the theoretical volume of nitrogen had been evolved and the reaction mixture was poured into 150 ml. of concd. ammonium hydroxide. By ether extraction and distillation there was obtained 9.0 g. (80%) of *m*-chlorophenylphenylacetylene, b.p. 153–155° at 3 mm. A redistilled center cut was taken for the hydration studies.

Anal. Calcd. for C₁₄H₉Cl: C, 79.1; H, 4.3; Cl, 16.7. Found: C, 79.3; H, 4.4; Cl, 16.5.

Diphenylacetylene. To a stirred mixture of 15 g. of benzil dihydrazone,¹³ m.p. 151–153°, 80 g. of silver trifluoroacetate, and 250 ml. of acetonitrile was added 70 ml. of triethylamine during 150 min. After 6 hr., 103% of the theoretical nitrogen had been evolved. After the mixture had been poured into 200 ml. of concd. ammonium hydroxide there was isolated 9.5 g. (85%) of diphenylacetylene, m.p. 58–60°.

Di-p-methoxyphenylacetylene. As in the case of diphenylacetylene di-*p*-methoxybenzil dihydrazone,¹³ m.p. 115–118°, was oxidized to di-*p*-methoxyphenylacetylene,¹⁴ m.p. 140–146°, in 85% yield. The pure acetylene melted at 145–146°, after two recrystallizations from 1:2 acetic acid-alcohol.

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(12) M. T. Clarke, E. C. Hendley, and O. K. Neville, *J. Am. Chem. Soc.*, **77**, 3280 (1955) report a m.p. of 86°.

(13) W. Schlenk and E. Bergmann, *Ann.*, **463**, 76 (1928).

(14) H. Wiechell, *Ann.*, **279**, 338 (1894) reported a m.p. of 142°.

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Reactions of Dipivaloyl with Organometallic Reagents¹

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Received November 4, 1957

Dipivaloyl (I) reacts with ethoxyethynylmagnesium bromide and ethoxyethynyllithium to yield 3-*t*-butyl-5,5-dimethyl-1-ethoxy-3-hydroxy-4-keto-1-hexyne (II). On treatment with acid II rearranges stereospecifically to yield ethyl *cis* 3-*t*-butyl-5,5-dimethyl-4-keto-2-hexenoate (V). Reaction of I with ethyl bromoacetate yields a hydroxyester (III) which, after hydrolysis and dehydration yields IV, the acid corresponding to V. IV is shown to exist in about equal amounts in the acyclic and cyclic forms, IV and VI.

In the hope of preparing intermediates suitable for conversion into *o*-di-*t*-butylbenzene, 2,2,5,5-

tetramethyl-3,4-hexanedione (I) (dipivaloyl) was treated with (I) ethoxyethynylmagnesium bro-

(1) Taken from the Ph.D. thesis of G. R. Kahle, Ohio State University, 1956.

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