oxidized to bianthrone and the latter, after isomerization in base, oxidized to the desired compound. The $\Delta^{10,10'}$-bianthrone was analyzed; calcd.: C, 87.5; H, 4.20. Found: C, 87.5; H, 4.17.

The helianthrone was prepared by the method of Scholl and Mansfeld[4] starting with α,α'-bianthraquinonyl. Efforts to prepare pure α,α'-bianthraquinonyl by the method of Scholl[5] were unsuccessful because a black powder was obtained from which it was not possible to separate the pure product by recrystallization from nitrobenzene or by continuous extraction with xylene. The α,α'-bianthraquinonyl was therefore prepared by the method of Ullmann and Minajeff[6] in a 75% yield (on recrystallization from nitrobenzene) from α-chloroanthraquinone.[7]

The procedure of Scholl and Mansfeld[4] was modified slightly by placing the mixture of helianthrone and copper dust in dilute nitric acid for 30 minutes to effect removal of the copper dust. Crystallization from xylene gave an equal mixture of yellow needles and red nuggets. These two forms melted with no decomposition at 294–297° compared to 296° reported by Sauvage[8] and had identical absorption spectra. A crude yield of about 80% was obtained which was reduced to 60% on recrystallization from xylene. The purified material was analyzed; calcd.: C, 88.0; H, 3.69. Found: C, 87.7; H, 3.7.

Pure mesonaphthobianthrone was easily prepared by the exposure of a solution of $\Delta^{10,10'}$-bianthrone in xylene to strong sunlight for 3 days.[2] The crude product was purified by recrystallization from nitrobenzene.

Absorption Spectra.—All absorption spectra were determined with a Beckman DU spectrophotometer using calibrated cells of path length 1.000 ± 0.001 cm. All measurements were made at room temperature.

Results

In Fig. 1 the absorption spectra of $\Delta^{10,10'}$-bianthrone, helianthrone and mesonaphthobianthrone in concentrated sulfuric acid are given.

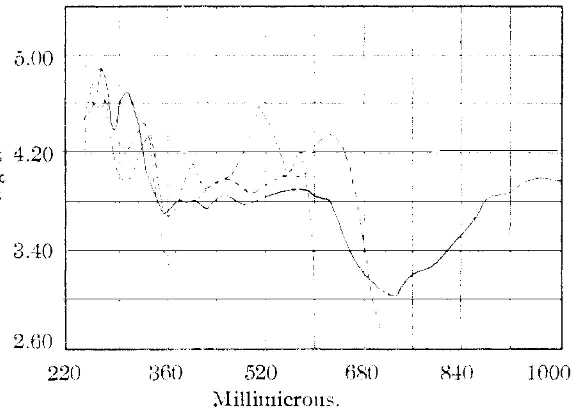


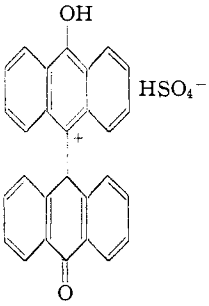
Fig. 1.—The absorption spectra of $\Delta^{10,10'}$-bianthrone, ——; helianthrone, —·—; and mesonaphthobianthrone in concentrated sulfuric acid, — — —.

Since the extinction coefficient changes with time, the absorption spectra were standardized for time as follows: the solutions were made up in dim light and the measurements were started 30 minutes after mixing with all measurements finished 80 minutes after mixing.

$\Delta^{10,10'}$-Bianthrone was reisolated from a sulfuric acid solution 80 minutes after mixing and analyzed by comparison of the absorption spectrum of the reisolated substance with the absorption spectrum of known $\Delta^{10,10'}$-bianthrone. No differences were noted in these spectra.

Discussion

The changes in color which occur on solution of these compounds in sulfuric acid, we believe, may be attributed to the formation of oxonium salts which are in resonance with structures that may be classed as triarylcarbonium ions and are analogs of the well known halochromic salts. Thus, the coördination of a proton on a carbonyl oxygen of $\Delta^{10,10'}$-bianthrone would give a hybrid consisting of fifteen charge-distributing polar structures among which Ia may be considered analogous to the halochromic salts. It is possible, of course, that the system may be doubly protonated. A cryoscopic examination of the system in pure sulfuric acid was made, but the data were inconclusive and not interpretable.



Ia

Coördination of other electrophillic agents might be expected to give rise to similar color phenomena. Indeed, stannic chloride in xylene and in nitrobenzene coördinates with I and II to afford colored complexes, although apparently not with III. The colors, however, are not as vivid as those produced by concentrated sulfuric acid.

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Synthesis and Properties of 1,2,5,6-Tetraphenylhexa-1,5-diene-3-yne

BY SHALOM ISRAELASHVILI AND JOLAN EDLITZ-PFEFFERMANN

RECEIVED APRIL 28, 1952

In an investigation on aryl substituted vinylacetylenes, we carried out the condensation of acetyldimagnesium bromide with desoxybenzoin. The product, 1,2,5,6-tetraphenylhexa-1,5-diene-3-yne (I), behaved like other derivatives of divinylacetylene[1]; the compound adds two molecules of maleic anhydride to yield the hydronaphthalene derivative (II) (or an isomer of it (IIa) produced by rearrangement of the double bonds). The hydrocarbon adds three molecules of bromine in the titration with 0.1 *N* potassium bromide–potassium bromate solution. However, bromination of (I), using carbon tetrachloride as a solvent gave a tetrabromide (probably produced by dehydro-

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(4) R. Scholl and J. Mansfeld, *Ber.*, **43**, 1734 (1910).

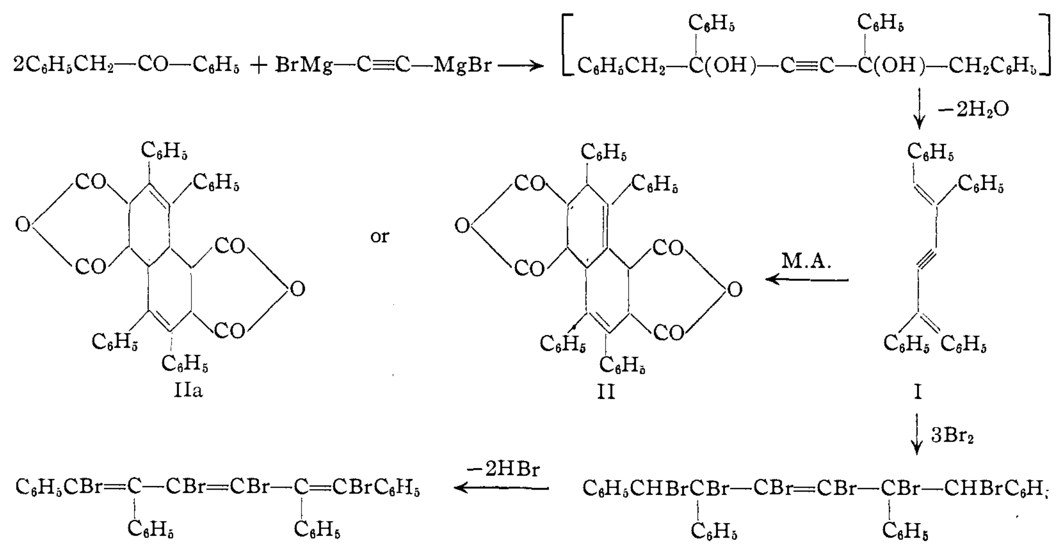
(5) R. Scholl, *ibid.*, **40**, 1691 (1907).

(6) F. Ullmann and V. Minajeff, *ibid.*, **45**, 687 (1912).

(7) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 128.

(8) G. Sauvage, *Ann. chim.*, **12**, 814 (1947).

(1) E. Dane, H. Höss, A. W. Bindseil and J. Schmitt, *Ann.*, **532**, 39 (1937); E. Dane, O. Höss, K. Eder, J. Schmitt and O. Schön, *ibid.*, **536**, 183 (1938); L. W. Butz and co-workers, *J. Org. Chem.*, **5**, 379 (1940), THIS JOURNAL, **63**, 3348, 3344 (1941); **64**, 1311 (1942).



halogenation of expected hexabromide). Catalytic hydrogenation was unsuccessful due to the very low solubility of (I).

The absorption spectrum (Fig. 1) resembles the spectrum of 1,6-diphenylhexatriene[2] and of α,β-di-(9-phenanthryl)-ethylene.[3]

Experimental[4]

Acetylenedimagnesium Bromide.—This was prepared according to the method of Jozitsch[5] by passing acetylene for five hours at 50 ml./min. through a stirred solution of 0.1 mole of ethylmagnesium bromide in 50 ml. of dry ether contained in a 250-ml., three-necked flask equipped with a mercury-sealed stirrer, reflux condenser, dropping funnel and gas inlet tube.

Condensation of Desoxybenzoin with Acetylene Digrignard.—After the acetylenedimagnesium bromide had stood overnight, a solution of desoxybenzoin (19.6 g., 0.1 mole) in dry ether (100 ml.) was added with stirring, over the course of three hours. Stirring was continued for another 20 hours and the mixture was allowed to stand for another 24 hours before it was hydrolyzed. The reaction mixture was poured into crushed ice and ammonium chloride, and the organic layer separated and filtered. After washing with carbonate solution, the ether solution was dried over magnesium sulfate and the ether removed. The resinous residue obtained was extracted with three 60-ml. portions of boiling ethanol, and the residue was treated separately (see below). After removing the solvent and starting materials from the ethanolic solution (distillation at reduced pressure), the residue crystallized in yellow-green needles from *n*-butyl acetate or dioxane; m.p. 201°, yield 5.2 g., 13.7%. Its solutions show a strong green fluorescence. It is sparingly soluble in ordinary organic solvents, but it is soluble in boiling benzene, xylene, *n*-butyl acetate and dioxane. It dissolves slowly in cold concd. sulfuric acid and gives a brown solution. The original product is recovered unchanged upon dilution with water.

Anal. Calcd. for $C_{30}H_{22}$: C, 94.2; H, 5.8. Found: C, 94.2; H, 5.9.

The insoluble product from the reaction mixture crystallized from dioxane in colorless rods of m.p. 184°; yield 1.0 g., 2.5%. This product did not respond to ketonic reagents. Catalytic hydrogenation in presence of Pd–BaSO$_4$ was unsuccessful. It dissolves in cold concentrated sulfuric acid and yields a deep-green solution.

Anal. Calcd. for $C_{28}H_{24}O_3$: C, 82.3; H, 5.8. Found: C, 82.5; H, 5.7.

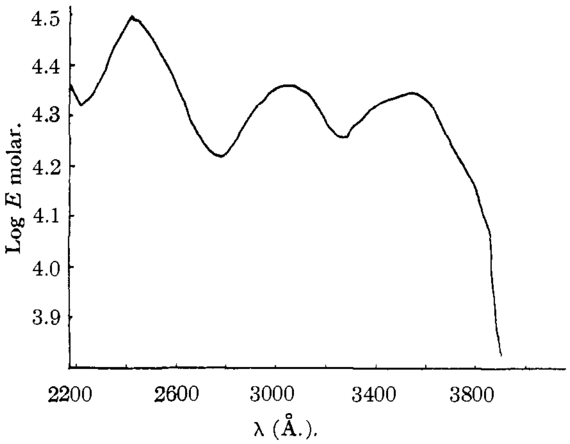


Fig. 1.—Ultraviolet absorption spectra of 1,2,5,6-tetraphenylhexa-1,5-diene-3-yne (solvent absolute ethanol).

Bromination of 1,2,5,6-Tetraphenylhexa-1,5-diene-3-yne.—The hydrocarbon absorbs three molecules of bromine in the titration with an 0.1 *N* solution of potassium bromide-potassium bromate.[6] Bromination of (I) in carbon tetrachloride solution gave the tetrabromide, which after two recrystallizations from isopropyl alcohol yielded colorless crystals, m.p. 125–126°.

Anal. Calcd. for $C_{30}H_{20}Br_4$: C, 51.4; H, 2.8; Br, 45.8. Found: C, 51.9; H, 2.7; Br, 45.4.

Reaction with Maleic Anhydride.—A mixture of the hydrocarbon (1 g.) and maleic anhydride (3 g.) was heated at 180° for three hours. The reaction mixture was poured into hot water, and the residue was dissolved in an aqueous potassium hydroxide solution, filtered, and the filtrate acidified with cold dilute sulfuric acid. The adduct was purified by dissolving in ethyl acetate and precipitating by adding excess carbon tetrachloride. It is soluble in hot acetone, dioxane, ethyl acetate and ethanol; insoluble in xylene, benzene, carbon tetrachloride and chloroform. After three purifications, a colorless product was obtained; m.p. 180–182°, yield 0.8 g., 40%.

Anal. Calcd. for $C_{38}H_{30}O_8 \cdot 5H_2O$: C, 64.8; H, 5.6; neut. equiv., 176. Found: C, 65.2; H, 5.4; neut. equiv., 182.

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[2] A. Smakula and A. Wassermann, *Z. physik. Chem.*, **A155**, 353 (1931); B. Arends, *Ber.*, **64**, 1936 (1931); M. Calvin and R. E. Buckles, THIS JOURNAL, **62**, 3324 (1940).

[3] R. N. Jones, *ibid.*, **67**, 1956 (1945); Y. Hirshberg and F. Bergmann, *ibid.*, **72**, 5118 (1950).

[4] M.ps. and b.ps. are uncorrected.

[5] I. Jozitsch, *Bull. soc. chim.*, [3] **32**, 552 (1904); G. Dupont, *Ann. chim. phys.*, [8] **30**, 485 (1913).

[6] Sidney Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 33–37.

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The Use of Dimethylformamide in the Ullmann Reaction

BY NATHAN KORNBLUM AND DAVID L. KENDALL[1]

RECEIVED JUNE 27, 1952

When a relatively reactive aryl halide is heated with copper powder in the absence of a solvent a vigorous, exothermic reaction may occur. In many instances it has, therefore, proved advantageous to add a diluent and for this purpose nitrobenzene has most often been used, although toluene, *p*-cymene, naphthalene, biphenyl and anthracene have also been employed.[2]

TABLE I

PREPARATION OF BIARYLS

Halide	Biaryl	Reaction time, hr.	M.p., °C.[a]	Yield, %[b]	Previous yield, %
2-Chloro-3-methoxynitrobenzene	2,2'-Dimethoxy-6,6'-dinitrobiphenyl	8	231–232	84[c]	70[d]
o-Chloronitrobenzene	2,2'-Dinitrobiphenyl	8	125.5–126	80	52–61[e]
2,5-Dichloronitrobenzene	4,4'-Dichloro-2,2'-dinitrobiphenyl	8	138–139	75	42[f]
m-Iodotoluene	3,3'-Dimethylbiphenyl	72	[g]	55	35[h]
p-Iodotoluene	4,4'-Dimethylbiphenyl	72	122–122.5	68	54[i]
Methyl *p*-iodobenzoate	4,4'-Dicarbomethoxybiphenyl	24	212–214	74[j]	70[k]
Methyl *m*-iodobenzoate	3,3'-Dicarbomethoxybiphenyl	72	103–104	89	60[l]
p-Iodophenetole	4,4'-Diethoxybiphenyl	72	176–177	77	72[m]
α-Iodonaphthalene	1,1'-Binaphthyl	24	159–159.5	76	68[n]

[a] All m.ps. determined on a Fisher–Johns hot-stage. [b] These are the yields of products which have been recrystallized to the melting points given in this Table. [c] Average of four runs. [d] R. Adams and G. C. Finger [THIS JOURNAL, **61**, 2828 (1939)]; m.p. 226–228° (uncor.). [e] R. C. Fuson and E. A. Cleveland [*Org. Syntheses*, **20**, 45 (1940)]; m.p. 123.5–124.5° (cor.). [f] F. Ullmann and J. Bielecki [*Ber.*, **34**, 2174 (1901)]; m.p. 136°. [g] B.p. 135° at 3 mm., n^{20}_{D} 1.5925; O. S. Mills [*Nature*, **167**, 726 (1951)] reports b.p. 130° at 1 mm., n^{20}_{D} 1.5962; N. Kornblum [*Org. Syntheses*, **21**, 30 (1941)] gives b.p. 115° at 3 mm., n^{20}_{D} 1.5945. [h] F. Ullmann [*Ann.*, **332**, 38 (1904)]. [i] F. Ullmann, *ibid.*; m.p. 122°. [j] When account is taken of the starting material which is recovered the yield rises to 93%; presumably a longer reaction time would be beneficial. [k] F. Ullmann, *ibid.*; m.p. 214°. [l] F. Ullmann, *ibid.*; m.p. 104°. [m] F. Ullmann, *ibid.*; m.p. 176°. [n] K. Brass and R. Patzelt [*Ber.*, **70**, 1349 (1937)]; m.p. 154°. C. Willgerodt and P. Schlosser [*Ber.*, **33**, 698 (1900)], report m.p. 160.5° (cor.).

Incidental to another investigation, it has now been found that dimethylformamide is a good solvent for the Ullmann reaction, in spite of the fact that its boiling point, 153°, is lower than that of most of the diluents previously used. Among other things, dimethylformamide has the considerable advantage over the previously employed diluents of being water soluble; hence it can easily be removed from the reaction product. Not only does this simplify the isolation procedure but, as can be seen from Table I, the yields are significantly higher than those obtained previously.

It should be emphasized that with those halides which are inert under the usual Ullmann conditions the present procedure offers no advantage. Thus, after 24 hours in refluxing dimethylformamide the following halides had undergone little or no reaction with copper powder: *p*-bromophenetole, *m*-chloronitrobenzene, *p*-chloronitrobenzene, *p*-bromonitrobenzene[3] and α-bromonaphthalene.

Experimental

The copper powder used was Natural Copper 44F (United States Bronze Powder Works) pretreated according to Kleiderer and Adams.[4] Dimethylformamide[5] (du Pont) was stored over calcium hydride at least 12 hours; very possibly no drying is necessary but this point was not investigated. The 2-chloro-3-methoxynitrobenzene (m.p. 94°) was prepared according to Finger.[6] *o*-Chloronitrobenzene was obtained from Monsanto and the other starting halides were Eastman Kodak Co. "white label" products.

The following preparation of 2,2'-dimethoxy-6,6'-dinitrobiphenyl is typical. In the other runs the only changes were in the time of reaction (*cf.* Table I) and the solvent used for recrystallizing the product. With a given biaryl the same solvent was employed as had been used by the workers cited in Table I.

Preparation of 2,2'-Dimethoxy-6,6'-dinitrobiphenyl.—Twenty grams of 2-chloro-3-methoxynitrobenzene and 100 ml. of dimethylformamide were placed in a 200-ml., 3-neck flask equipped with reflux condenser and a tantalum Hershberg-type stirrer. The solution was heated to reflux and then 20 g. of copper powder was added in one portion. Heating at reflux was continued for four hours after which another 20-g. portion of copper powder was added; refluxing was continued for a second four-hour period. On cooling, the reaction mixture was poured into two liters of water and then filtered. The solids were extracted with a total of two liters of boiling acetone. Concentration of the acetone extracts gave 11.1 g. of yellow crystals melting at 231–232° (uncor.); further evaporation of the acetone, followed by the addition of absolute ethanol, gave another 2.8 g., m.p. 228–229°. The 2.8 g. was digested for 10 minutes on the steam-bath with about 5 ml. of glacial acetic acid. After cooling to room temperature the crystals were isolated by filtration and then washed with a little glacial acetic acid. In this way a small amount of copper salts was removed leaving 2.4 g. of the dimethoxydinitrobiphenyl, m.p. 231–232° (uncor.), total yield 13.5 g. (84%).

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[1] Atomic Energy Commission Predoctoral Fellow 1950–1952.

[2] P. E. Fanta, *Chem. Revs.*, **38**, 149 (1946).

[3] W. Davey and R. W. Latter (*J. Chem. Soc.*, 264 (1948)) obtained no dinitrobiphenyl on treating *m*- or *p*-chloronitrobenzene with copper powder either in the absence of solvent (at 200–220°) or in refluxing nitrobenzene. With *p*-bromonitrobenzene a 15% yield of 4,4'-dinitrobiphenyl was obtained after nine hours in refluxing nitrobenzene. In the absence of a solvent *p*-bromonitrobenzene gave the biaryl in 36% yield after 40 minutes at 200–220°.

[4] E. C. Kleiderer and R. Adams, THIS JOURNAL, **55**, 4219 (1933).

[5] We wish to thank the Grasselli Division of E. I. du Pont de Nemours & Co., Inc., for a generous supply of dimethylformamide.

[6] G. C. Finger, Ph.D. Thesis, University of Illinois, 1938, p. 56.