figuration of which were established by its optical inactivity and its behavior with sodium metaperiodate.

Improved procedures are given for the preparation of α- and β-D-xylopyranose tetrabenzoates, 2,3,4-tribenzoyl-α-D-xylopyranosyl bromide and 2,3,4-tribenzoyl-2-hydroxy-D-xylal. The latter compound was found resistant to hydrogenation under the conditions employed for the reduction of its acetyl analog. Revised physical constants for some of the substances are recorded.

BETHESDA, MARYLAND RECEIVED DECEMBER 12, 1946

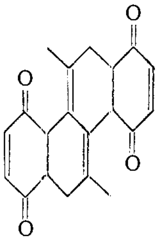
[CONTRIBUTION FROM THE BUREAU OF ANIMAL INDUSTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Synthesis of Condensed Ring Compounds. XVI.[1] The Addition of Quinones to a Dienyne[2]

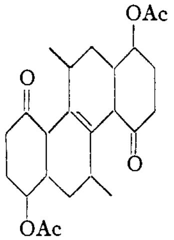
BY LEWIS W. BUTZ, ADAM M. GADDIS AND ELEANORE W. J. BUTZ

2,5-Dimethyl-1,5-hexadien-3-yne reacts with two moles of *p*-benzoquinone at 130° to give a brilliant yellow crystalline compound. Absorption in the ultraviolet was $\lambda_{max.}$ 2250 Å., ε 30000; inflection 2900 Å., ε 700; $\lambda_{max.}$ 3500 Å., ε 340. Hydrogenation at room pressure and temperature in the presence of platinum oxide–palladium oxide catalyst gave a decahydro derivative which formed a diacetate.

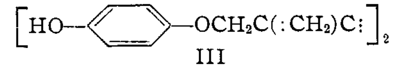
By analogy with other dienyne double additions[3] structure I can be considered for the yellow compound $C_{20}H_{18}O_4$. The properties are in good agreement with this formulation. The diacetate of the decahydro derivative, which showed no absorption in the ultraviolet characteristic of conjugation, is probably one of the diacetoxydimethyl-8-chrysitenediones, II. Open chain structures for the adduct, such as III, would appear to be excluded on the basis of the properties.



I



II



III

2,5-Dimethyl-1,5-hexadien-3-yne combined with one mole of tetrachloro-*p*-benzoquinone at room temperature to give a nearly colorless crystalline compound which dissolved in cold aqueous sodium hydroxide. Acidification of this alkaline solution with hydrochloric acid precipitated a white substance. In the ultraviolet the adduct showed $\lambda_{max.}$ 2720 Å., ε 8600 which is characteristic of phenols.[4]

Experimental[5]

Reaction of 2,5-Dimethyl-1,5-hexadien-3-yne with *p*-Benzoquinone.—Two and a half grams of freshly sublimed quinone and 2.45 g. of dienyne[6] were heated together without solvent in a sealed Pyrex tube, filled with carbon dioxide, at 130° for two hours. The resulting mixture was extracted with 200 ml. of ether. Eighty per cent. of the quinone taken was recovered from the ether extract. The brown solid residue (115 mg., 3%) of crude adduct melted at 214–216°. Recrystallization of 655 mg. of such crude adduct, which is quite insoluble in many common solvents, by continuous extraction with acetone and cooling gave 421 mg. of brilliant yellow crystals, m. p. 225–228° (dec. 219°).

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6. Found: C, 74.5; H, 5.7.

The compound was dissolved in dioxane for observation of the ultraviolet absorption spectrum.

The Decahydro Derivative of the Adduct.—Seventy milligrams of dimethylhexadienyne-*p*-benzoquinone adduct in 20 ml. of acetic acid (distilled from permanganate) was hydrogenated in the presence of 25.5 mg. of Adams catalyst containing 4% of palladium oxide. Four moles of hydrogen were taken up during the first hour and 0.9 mole during the next two hours. Filtration of the catalyst, removal of the acetic acid at 40–50° and 15 mm., and recrystallization of the residue from benzene gave 39.5 mg. of a colorless substance, m. p. 237–239° (in evacuated tube). No absorption was found in the ultraviolet at 2200–3000 Å. In anticipation of partial acetylation during the hydrogenation, the product was acetylated before analysis by refluxing with 2 ml. of pyridine and 1 ml. of acetic anhydride for twenty-five minutes. After working up as usual, the product was recrystallized first from hexane containing 1% of benzene and then from ether. The colorless product, which melted at 238–240° (evacuated tube), is probably the diacetate II.

Anal. Calcd. for tetraacetate, $C_{28}H_{36}O_8$: C, 67.2. Calcd. for diacetate, $C_{24}H_{32}O_6$: C, 69.2; H, 7.7. Found: C, 68.9; H, 7.6.

Reaction of 2,5-Dimethyl-1,5-hexadien-3-yne with Tetrachloro-*p*-benzoquinone.—Seventeen grams of the quinone was dissolved in 330 ml. of boiling benzene and the solution was cooled rapidly. Two moles (14.5 g.) of the dienyne and 1 ml. of 33% aqueous trimethylamine[7] were added and the mixture was shaken at 40° for ten days. Thereafter it was allowed to stand in the sunlight[7] at room temperature for two days. Five and a half grams of unchanged tetrachloro-*p*-benzoquinone was removed from the mixture of products by filtration, the filtrate was evaporated to dryness, and the residue was taken up in 150 ml. of boiling Skellysolve "C" (heptanes).

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[1] For preceding paper see THIS JOURNAL, 69, 117 (1947).

[2] This work was supported by an allotment from the Special Research Fund (Bankhead-Jones Act of June 29, 1935). Not subject to copyright.

[3] Butz and Joshel, THIS JOURNAL, 64, 1311 (1942), and earlier papers.

[4] Schjånberg, *Svensk Kem. Tid.*, 52, 185 (1940).

[5] Melting points are corrected. Analyses by Arlington Laboratories, Fairfax, Virginia.

[6] Butz, Gaddis, Butz and Davis, *J. Org. Chem.*, 5, 379 (1940).

[7] Albrecht, *Ann.*, 348, 45 (1906).

Cooling and removal of 4 g. more of tetrachloroquinone gave a red solution. This was boiled with charcoal for two hours. The resulting pale yellow solution was evaporated, finally at 50° and 80 mm., to remove dienyne. The residue, which crystallized, was recrystallized from 5 ml. of ethanol to give 300 mg. of nearly colorless substance, m. p. 75–78°.

Anal. Calcd. for $C_{14}H_{10}O_2Cl_4$: C, 47.7; H, 2.8. Found: C, 48.0; H, 2.8.

The compound was dissolved in ethanol for observation of the ultraviolet absorption.[8] About 20 mg. dissolved in cold aqueous sodium hydroxide (one pellet in 4 ml.) in fifteen minutes.

Summary

1. 2,5-Dimethyl-1,5-hexadien-3-yne has been combined with *p*-benzoquinone to give a compound, $C_{20}H_{18}O_4$. This gave a decahydro compound which is probably a derivative of 8-chrysitene.

2. 2,5-Dimethyl-1,5-hexadien-3-yne and tetrachloro-*p*-benzoquinone combined mole for mole to give a crystalline adduct.

BELTSVILLE, MARYLAND RECEIVED SEPTEMBER 13, 1946

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[8] We are indebted to Mr. H. Bastron and Dr. R. E. Davis for the ultraviolet absorption data in this paper.

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

Derivatives of Methylphenylarsine[1]

BY E. J. CRAGOE, JR., R. J. ANDRES, R. F. COLES, BILL ELPERN, J. F. MORGAN AND CLIFF S. HAMILTON[1a]

Derivatives of mixed aliphatic–aromatic arsenicals have generally been limited to those readily prepared, such as arsinic acids, chloroarsines, bromoarsines and hydroxyarsines. It was thought worth while to prepare a series in which the chloro, bromo, cyano, thiocyano, methoxy and acetoxy derivatives could be compared for toxicity purposes. Except for the acetoxy derivative, individual examples of the various types are listed in the literature. Since no general methods of synthesis were available, each member was prepared by the easiest route. Methylphenylarsine and methyl-(3-nitrophenyl)-arsine were chosen as basic nuclei for the study.

Methylphenylchloroarsine was first prepared by the method of Burrows and Turner.[2] It was later found that methyl sulfate could be substituted for methyl iodide in the preparation of methylphenylarsinic acid, simplifying the procedure considerably. The cyano, thiocyano, acetoxy and methoxy derivatives were prepared from the chloro compound by metathesis with appropriate salts. Methylphenylarsine was obtained by an adaptation of the reduction procedure of Palmer and Adams.[3] Attempts to prepare a chloroacetoxy compound failed.

Methyl-(3-nitrophenyl)-arsinic acid has not been previously reported. It was most conveniently prepared from 3-nitrobenzenediazonium sulfate and methyldichloroarsine. Nitration of methylphenylarsinic acid also gave appreciable yields of the desired product but the Meyer reaction of methyl sulfate and 3-nitroarsenosobenzene resulted in only sufficient material for identification purposes. Methyl-(3-nitrophenyl)-arsinic acid was reduced to the corresponding chloroarsine and the latter converted to the cyano derivative. The bromoarsine was also prepared but the reductive properties of sodium methoxide and amalgamated zinc toward the nitro group prevented the preparation of the arsine and the methoxy derivative.

Experimental

Methylphenylarsinic Acid.—Phenyldichloroarsine (111 g., 0.5 mole) was added slowly with stirring to a solution of sodium hydroxide (96 g., 2.4 mole) in water (200 ml.), the solution cooled and placed in a 3-necked flask equipped with dropping funnel, stirrer and condenser. Methyl sulfate (78 g., 0.62 mole) was added, dropwise, with stirring, keeping the temperature between 20 and 30°. After stirring overnight, the temperature was raised to 80° for one hour. The precipitated salts were filtered off, the filtrate evaporated to 250 ml. and made neutral to litmus paper with sulfuric acid (18 *N*). The solution was treated with absolute ethanol (250 ml.) and filtered. The filtrate was made acid to congo red paper with sulfuric acid (18 *N*), the precipitated salts removed and the residual solution concentrated to 200 ml. After dilution with absolute ethanol (600 ml.), the salts which separated were removed and the ethanol solution evaporated to dryness. The salt fractions were washed out with acetone and the acetone solution also evaporated. The combined yield from the ethanol and acetone fractions was 97 g. (97%). This product was reduced to the chloroarsine by the method of Burrows and Turner.[2]

Methylphenylcyanoarsine.—Methylphenylchloroarsine (87 g., 0.43 mole) was added slowly with stirring to a solution of sodium cyanide (23 g., 0.47 mole) in water, keeping the temperature at 20–25°. After the heat of reaction had been dissipated the stirring was continued for thirty minutes. The oily layer was separated and the aqueous layer extracted twice with 50-ml. portions of benzene. The benzene extract and oil were combined, washed with 100 ml. of water, dried over calcium chloride and distilled.

Methylphenylmethoxyarsine.—Sodium (10 g., 0.435 mole) was dissolved in anhydrous methanol (150 ml.) in a 3-necked flask equipped with dropping funnel, stirrer and condenser. Calcium chloride tubes were used to prevent the absorption of moisture. Methylphenylchloroarsine (75 g., 0.37 mole) was added slowly with stirring and then the reaction mixture heated at reflux for thirty minutes. The precipitated salt was removed and the alcohol removed under reduced pressure. The residue was

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[1] The work herein described was done under Contract OEMsr-85, recommended by the National Defense Research Committee between the Office of Scientific Research and Development and the Board of Regents of the Univeristy of Nebraska.

[1a] Official investigator.

[2] Burrows and Turner, *J. Chem. Soc.*, **119**, 1373 (1921).

[3] Palmer and Adams, THIS JOURNAL, **44**, 1356 (1933).