Methylol-1,2-cyclopentano-decalin (9 g.) was hydrogenated over 4 g. of nickel-on-alumina for eight hours at 325° to give a 79% yield of 2-methyl-1,2-cyclopentano-decalin. 2-Methyl-1,2-cyclopentanoperhydrophenanthrene was prepared from the methylol compound under the conditions just stated.

Summary

A number of derivatives of 1,2-cyclopentanohydronaphthalenes and of 1,2-cyclopentanohydrophenanthrenes, with a substituent in an angular position, have been prepared by development of the methods of Bardhan, Sengupta, Kon, Bougault, Bogert and Cook. The use of liquid hydrogen fluoride at 0° has made possible the cyclization in excellent yields of certain substituted β-keto esters with the formation of 1,2-cyclopentenodihydronaphthalenes and phenanthrenes, with a carbethoxy group in an angular position. The carbethoxy group in these compounds has been reduced to methylol and methyl groups. Derivatives of chrysene have been prepared by a modified Bogert–Cook synthesis. A practical synthesis of 1-methyl-2-alkylnaphthalenes from 2-naphthol has been illustrated.

MADISON, WISCONSIN RECEIVED DECEMBER 10, 1948

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE AND THE POLYTECHNIC INSTITUTE OF BROOKLYN]

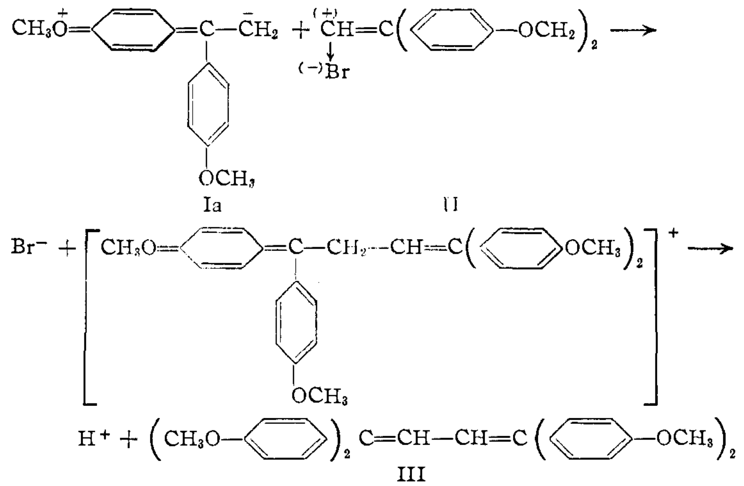
1,1,4,4-Tetraanisyl-1,3-butadiene

BY FELIX BERGMANN, JACOB SZMUSZKOWICZ AND ELCHANAN DIMANT[1]

Although 1,1-diphenylethylene can be dimerized by a variety of agents,[2] no success attended experiments to dimerize 1,1-di-(*p*-anisyl)-ethylene (I).[3] However, when we tried to convert (I) into the corresponding vinyl bromide (II) in acetic acid solution, we obtained a light-yellow substance of m. p. 207°, which we considered previously to be a "dimer."[4] Addition of sodium acetate to the bromination mixture prevented the formation of the yellow compound and stopped the reaction at the intermediate stage (II).

We have now found that the substance of m. p. 207° is not a dimer, but represents 1,1,4,4-tetraanisylbutadiene (III).[5] Proof of this structure can be given in the following way: (a) All unsaturated dimers of diarylethylenes represent butenes[2] and consequently absorb one mole of hydrogen. Compound (III) however takes up two moles of hydrogen. (b) Reaction of (II) with Grignard magnesium gives (III), in analogy to the synthesis of 1,1,4,4-tetraphenylbutadiene.[6] (c) The absorption spectrum of (III) is similar to that of 1,1,4,4-tetraphenylbutadiene (see Fig. 1).[7] Moreover, as in the latter compound, V, the spectrum remains unchanged after three hours of irradiation indicating a structure in which there is no possibility of a *cis–trans* transformation.

The direct formation of (III) during the bromination of dianisylethylene is probably to be interpreted in the following way



If this explanation is correct, then (I) and (II) should react with each other to form (III). This reaction was found to proceed smoothly at 120° and to give a quantitative yield of (III). The above reaction scheme also explains why (I) cannot be dimerized by strong acids: The intermediate carbonium ion $R_2{}^+CCH_3$, because of resonance stabilization through the *p*-methoxy group, cannot attack the β-carbon of a second ethylene molecule. In the formation of the butadiene (III) the resonance form (Ia) acts as a nucleophilic agent, directly substituting the β-bromine atom. Experiments now under hand will show whether this reaction presents a general method for the synthesis of 1,1,4,4-tetraarylbutadienes.[8]

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[1] Part of a thesis, submitted to the Hebrew University, Jerusalem, 1949.

[2] Staudinger and Kon, *Ann.*, **384**, 38 (1911); E. Bergmann and Weiss, *ibid.*, **480**, 49 (1930).

[3] Schmitz-Dumont, Thömke and Diebold, *Ber.*, **70**, 175 (1937).

[4] F. Bergmann and Szmuszkowicz, THIS JOURNAL, **69**, 1777 (1947).

[5] The analytical figures for a dimer of I ($C_{32}H_{32}O_4$—calcd., C, 80.0; H, 6.7) and for III ($C_{32}H_{30}O_4$—calcd., C, 80.3; H, 6.3) are too near to permit a distinction between these two structures.

[6] Lipp, *Ber.*, **56**, 571 (1923).

[7] Hirschberg, Bergmann and Bergmann, in preparation.

[8] *E. g.*, 1,1,4,4-tetraphenylbutadiene is obtained likewise by direct interaction of 1,1-diphenylethylene with 1,1-diphenylvinyl bromide. However, due to the absence of the activating *p*-methoxy groups the conditions of this reaction are much more drastic than in the synthesis of tetraanisylbutadiene. These and other experiments will be reported in a forthcoming paper.

Experimental

1. **Dianisylvinyl Bromide and Magnesium.**—Because of the difficulty to induce the grignardization of this bromide we used the entrainment method:

A Grignard solution was prepared from dianisylvinyl bromide (1.6 g.), methyl iodide (0.7 g.) and magnesium (0.27 g.) in ether (40 cc.). After one hour of reflux 3 g. of (II) was added and the mixture was again refluxed for thirty-six hours. A yellow precipitate formed in the mixture. After treatment with dilute sulfuric acid the yellow material was filtered off and washed with ether; m. p. 204°, yield 0.85 g. (25%). Recrystallization from butyl acetate gave yellow needles of m. p. 206-207°, which showed no m. p. depression upon admixture of (III). No attempt was made to isolate the ether-soluble reaction products.

2. **Catalytic Reduction of 1,1,4,4-Tetraanisylbutadiene.**—The diene (1.2 g.), suspended in ethyl acetate (40 cc.), absorbed 155 cc. of hydrogen in the presence of Adams platinum oxide (0.5 g.) within two hours (calcd. for 31°, 755 mm., 164 cc.). The oily reduction product crystallized after treatment with *n*-hexane and was obtained from a benzene-methanol mixture as white rods of m. p. 121°; yield, 1.1 g.

Anal. Calcd. for $C_{32}H_{34}O_4$: C, 79.67; H, 7.05. Found: C, 79.64; H, 7.12.

3. **Condensation of Dianisylethylene and Dianisylvinyl Bromide.**—The bromide (640 mg.) and the ethylene (480 mg.) were thoroughly mixed and heated in an oil-bath with the exclusion of moisture. The mixture melts at 100-110° and gives off fumes of hydrogen bromide. After a few minutes it resolidifies. It was kept at 120° for ten hours and then treated with butyl acetate; yield 0.95 g. (quantitative), m. p. 203-204°. Recrystallization from the same solvent gave yellow rods of m. p. 206-207°, identical with the two previous preparations of (III).

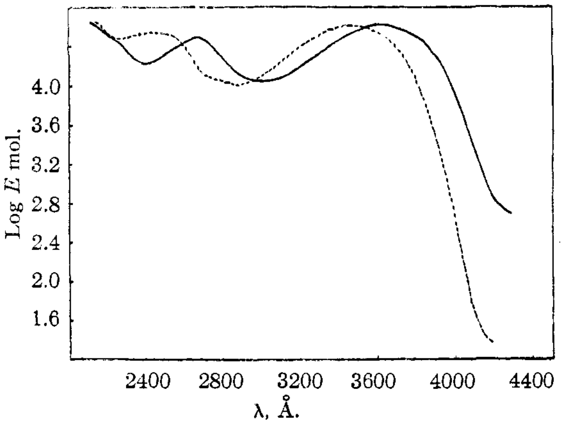

Fig. 1.—Ultraviolet absorption spectrum of — 1,1,4,4-tetraanisylbutadiene, ------ 1,1,4,4-tetraphenylbutadiene.

4. **Absorption Spectra.**—The spectra were measured in 95% ethanol by a Beckman quartz spectrophotometer.

Summary

The so-called "dimer," obtained in the bromination of dianisylethylene, is shown to be 1,1,4,4-tetraanisylbutadiene. The same substance can be prepared by interaction of dianisylethylene and dianisylvinyl bromide. The mechanism of this reaction is discussed.

RECHOVOT, ISRAEL
BROOKLYN, N. Y.

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[CONTRIBUTION NO. 175 FROM THE RESEARCH LABORATORIES OF HOFFMANN-LA ROCHE, INC.]

3-Pyridols in the Mannich Reaction[1]

BY ARTHUR STEMPEL AND ELAINE C. BUZZI

The Mannich reaction with phenols has recently been extended to 3-pyridols in attempts to prepare pyridoxine,[2] its analogs,[3] and antagonists.[4] A Mannich type of reaction employing sodium hydroxide instead of organic amines for the direct introduction of hydroxymethyl groups in 3-pyridols has also been reported.[5] Since the directive influence of the phenolic group has been studied only in cases where the ortho position is unsubstituted,[5] the following investigation of the scope and direction of the Mannich reaction with 3-pyridols was undertaken.

The substituted 3-pyridol reacted rapidly with formaldehyde and dialkylamines, alkarylamines, and heterocyclic amines such as piperidine and morpholine to give 2-(substituted amino)-methyl-3-pyridols in good yield. In all cases, the products were most readily isolated by distillation *in vacuo*. Where the products were solid, purification by distillation was still preferable to crystallization. The basic pyridols appear to be stable to heat with the exception of 2-di-*n*-butylaminomethyl-3-pyridol which showed signs of decomposition during distillation. Although attempts to prepare an analytically pure crystalline dihydrochloride of this compound were unsuccessful, it has been included since, in work to be reported at a later date, an ester of the correct analysis has been isolated. In general, these compounds have been characterized as the dihydrochlorides. The side chain basic group reacts readily with one mole of methyl bromide in the cold to give nicely crystalline quaternary salts. Quaternization of the pyridine nitrogen requires higher temperatures. Compounds of this type are listed in Table I.

By the catalytic debenzylation of 2-(N-methylbenzylaminomethyl)-3-pyridol, 2-methylaminomethyl-3-pyridol was readily prepared. In this manner, by the selection of the proper N-sub-

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[1] Presented at the Meeting-in-Miniature of North Jersey Section, American Chemical Society, January 10, 1949.

[2] Perez-Medina, Mariella and McElvain, THIS JOURNAL, **69**, 2574 (1947).

[3] Brown and Miller, *J. Org. Chem.*, **11**, 388 (1946).

[4] (a) Martin, Avakian and Moss, *J. Biol. Chem.*, **174**, 495-500 (1948); (b) Martin and Avakian, U. S. Patent 2,455,259, November 30, 1948.

[5] Urbanski, (a) *J. Chem. Soc.*, 1104-1105 (1946); (b) 132-134 (1947).