6 N sulfuric acid solution was slowly added. Ethyl ether was added, as before, and the solids separating were collected and dried. Sublimation of the 2.5 g. of crude products so obtained yielded 0.7 g. of 4,4'-dimethoxybiphenyl at a bath temperature up to 150° (0.005 mm.) and 0.1 g. of impure 4,4"-dimethoxyterphenyl up to 280°. The residue was infusible. The terphenyl fraction was recrystallized three times from toluene but still softened at 268° and was not entirely fused at 285° though most melting occurred at 275°. The presence of higher-melting impurities is thus indicated, probably the analogous dimethoxyquaterphenyls or even higher members.

Summary

4',4"-Dihydroxy-*o*-terphenyl and 4,4"-dihydroxy-*p*-terphenyl, the dimethyl ethers and diacetates have been prepared and characterized.

The reaction between 4,4'-dimethoxybiphenyl and *p*-methoxyphenylmagnesium bromide has been found to form small amounts of 4,4"-dimethoxy-*p*-terphenyl.

URBANA, ILLINOIS RECEIVED DECEMBER 22, 1943

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Pinacols and Pinacolone from *p*-Methoxyacetophenone

BY CHARLES C. PRICE AND GEORGE P. MUELLER[1]

The successful dehydration of the pinacols from acetophenone[2,3] and *p*-hydroxyacetophenone[4] to the corresponding butadiene prompted an attempt to carry out a similar conversion for the two stereoisomeric pinacols from *p*-methoxyacetophenone. In every instance, however, dehydration resulted in rearrangement to the pinacolone.

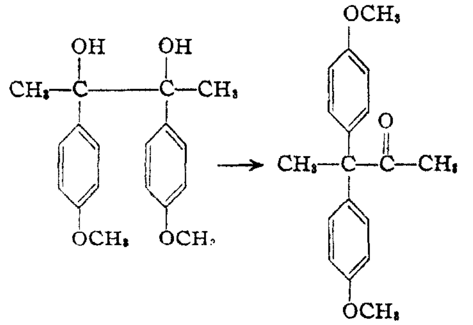
p-Methoxyacetophenone pinacol was prepared in 90% yields by electrolytic reduction of the ketone in potassium acetate, water and alcohol.[5] The crude product, upon repeated recrystallization from methyl alcohol or glacial acetic acid, gave the low- and high-melting isomers, respectively. The low-melting isomer showed some tendency toward solvate formation, the analyses of the compound indicating one-half molecule of methanol present before intensive drying. Also, recrystallization of this isomer, m. p. 122–123°, from ethylene glycol gave material melting at 111–113°; one recrystallization from methanol restored the melting point to its former value. The higher-melting isomer, m. p. 168–169°, was also obtained upon reduction of the ketone by aluminum amalgam in moist ether.

Oxidation of the low-melting isomer with lead tetraacetate yielded *p*-methoxyacetophenone, which was isolated quantitatively as the phenylhydrazone.

Several unsuccessful attempts were made to dehydrate this pinacol. Fraser[3] studied the yields obtained upon dehydration of acetophenone pinacol with acetyl chloride in terms of the time of reaction and found seven minutes at reflux with an equal weight of the acid chloride to be the optimum conditions. Such a reaction carried out with *p*-methoxyacetophenone pinacol (with a trace of hydroquinone present to inhibit polymerization) produced 74% of the pinacolone rather than the diene. A crystal of iodine dropped into the melted pinacol at 150° caused vigorous gas-evolution. The oil realized upon cooling did not show positive reactions either for an unsaturated or ketone derivative.

Both isomeric pinacols were treated repeatedly with fused sodium acetate in acetic anhydride, acetic anhydride and dry pyridine, and the high-melting isomer with benzoyl chloride and sodium hydroxide, but in no instance was esterification of the hydroxyl groups achieved. Any attempt to esterify these groups by an acidic reagent resulted in pinacolone rearrangement.

This rearrangement was conveniently carried out at room temperature in acetic anhydride, a trace of sulfuric acid serving as the catalyst. By analogy with 4,4-dianisyl-3-hexanone, which was obtained upon rearrangement of *p*-methoxypropiophenone-pinacol,[6] it was anticipated that this pinacolone should be 3,3-dianisyl-2-butanone.



This pinacolone did not undergo the iodoform reaction as modified by Fuson and Tullock.[7] This was not conclusive evidence for the absence of the acetyl grouping, however, for Poggi[8] has shown that pinacolone itself would not undergo the iodoform reaction when the procedure of Lieben[9] was

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(1) Eli Lilly and Company Fellow, 1941–1943.

(2) Allen, Eliot and Bell, *Can. J. Research*, **17B**, 75 (1939).

(3) Fraser, Thesis, *University of Illinois*, 1939.

(4) Dodds, Golberg, Lawson and Robinson, *Proc. Roy. Soc.* (London), **127B**, 140 (1939).

(5) We are indebted to Professor Sherlock Swann of the Department of Chemistry for the preparation of this pinacol and to Mr. H. D. Marshall and Mr. H. Kerfman, who carried out the electrolytci reductions under his direction.

(6) Wessely, Kerschbaum, Kleedorfer, Prillinger and Zajic, *Monatsh.*, **73**, 127 (1940).

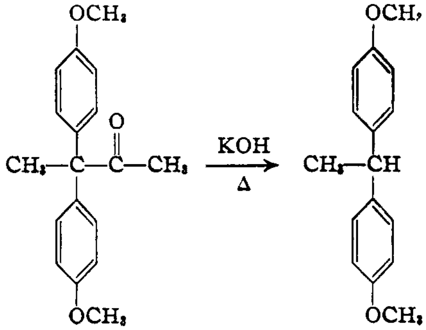
(7) Fuson and Tullock, THIS JOURNAL, **56**, 1638 (1934).

(8) Poggi, *Atti soc. ital. progresso sci.*, XXI Riunione, **2**, 576 (1933).

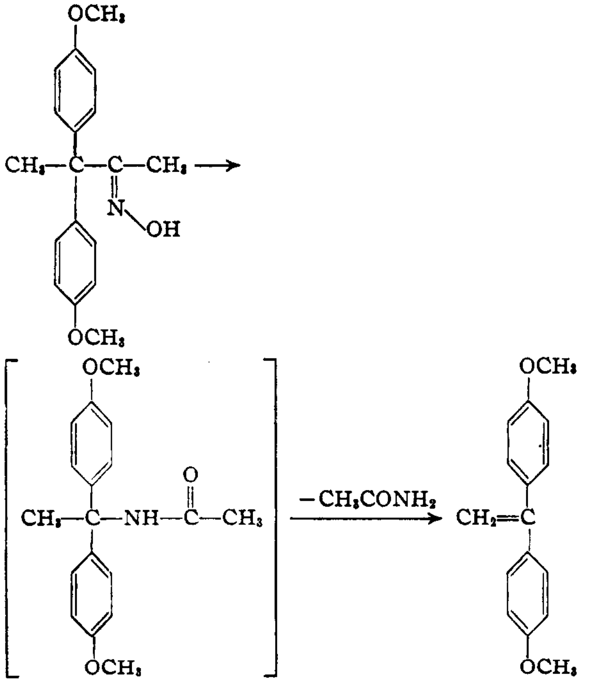
(9) Lieben, *Ann.*, VII Supplementband, 218 (1870).

used. Fuson and Tullock observed that pinacolone would undergo the reaction in dioxane solution but that a longer period of heating was necessary.

The ketone was cleaved by molten potassium hydroxide to give a compound having the composition of 1,1-dianisylethane, m. p. 72°. The melting point of this compound has been reported as 59.4° by Lunjak.[10]



The oxime of 3,3-dianisyl-2-butanone was prepared. It proved to be insoluble in alkali. When shaken with phosphorus pentachloride in dry ether this oxime apparently underwent a Beckmann rearrangement. The product, m. p. 141–143°, contained no nitrogen, but showed definite unsaturation. It proved to be 1,1-dianisylethene.[11]



Experimental[12]

2,3-Dianisyl-2,3-dihydroxybutane.—Apparatus for the electrolytic reduction[13] consisted of a 400-cc. beaker, which formed the anode compartment, the anode itself being a sheet of metal bent into a cylinder to fit around an alundum cup which formed the cathode compartment. A rubber stopper fitting into this cup carried the cathodes and an Allihn condenser. In all reductions the area of the cathode was 100 sq. cm. and the total current 2 amp., making the density 0.02 amp. per sq. cm. The combinations of lead anode and cathode or of tin cathode and iron anode were found to be quite satisfactory.

p-Methoxyacetophenone, 20 g., was introduced into a catholyte consisting of 30 g. of potassium acetate, 55 cc. of ethyl alcohol and 25 cc. of water. This mixture was placed in the alundum cup. In some experiments two equivalents of ethyl acetate were added to neutralize the alkali liberated during the reduction. The anolyte consisted of a 40% aqueous solution of potassium carbonate. A current was passed at 110 v. until 120% of the theoretical amount had been used. The entire reduction took place at the refluxing temperature of the catholyte. The catholyte was poured into a liter of cold water and the oil precipitating gradually crystallized and was collected on a filter. The yield of this crude product was 18 g. or 90%. In another experiment where 33 g. of the ketone was reduced in the presence of ethyl acetate the crude product was steam distilled, giving 27 g. of product. The crude material from the first reduction melted at 114–135°.

Repeated recrystallization of the crude product from methyl alcohol gave the low-melting form, m. p. 122–123°. This isomer was quite soluble in glacial acetic acid.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.50; H, 7.34. Found: C, 71.10; H, 7.50.

Similar treatment of the crude pinacol with glacial acetic acid, or even one recrystallization therefrom followed by repeated recrystallization from ethyl alcohol, yielded the high-melting form, m. p. 168–169°.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.50; H, 7.34. Found: C, 71.16; H, 7.22.

Approximately 3 g. of amalgamated, granulated aluminum, 5 g. of *p*-methoxyacetophenone and 30 cc. of moist ether were shaken in a flask for three days, after which the ether was evaporated and the residue warmed with methyl alcohol and filtered. The solution deposited a few crystals of a compound, m. p. 162–165°, which did not depress the melting point of the high-melting isomer obtained above.

Oxidation with Lead Tetraacetate.—The low-melting pinacol, 1.51 g. (0.005 mole), was suspended in 10 cc. of glacial acetic acid and 2.25 g. (0.005 mole) of lead tetraacetate was added to the mixture. After both reactants had dissolved, addition of 1.5 g. of phenylhydrazine in 5 cc. of glacial acetic acid immediately precipitated 2.56 g. of orange *p*-methoxyacetophenone phenylhydrazone. After three recrystallizations from ethyl alcohol it melted at 136–138° (dec.) and did not depress the melting point of an authentic sample of the hydrazone. This derivative decomposed upon standing for three days at room temperature.

Pinacolone Rearrangement: 3,3-Dianisyl-2-butanone.—On addition of one drop of sulfuric acid, 0.5 g. of the low-melting pinacol suspended in 2.5 cc. of acetic anhydride dissolved immediately. Water precipitated the pinacolone which was recrystallized several times from ethyl alcohol, m. p. 69.7–71.5°. The high-melting isomer behaved likewise and yielded the same product. From 7.0 g. of the crude mixture of pinacols, 4.1 g. or 63% of the theoretical amount of the pinacolone was realized.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.14; H, 7.27.

The **oxime** was insoluble in strong alkali and was recovered unchanged following two hours of heating in a sealed tube at 100° with concentrated hydrochloric acid. It crystallized from a large volume of ethyl alcohol in fine, colorless needles, m. p. 192–194°.

Anal. Calcd. for $C_{18}H_{21}O_3N$: C, 72.22; H, 7.07. Found: C, 71.75; H, 6.95.

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(10) Lunjak, *J. Russ. Phys.-Chem. Soc.*, **36**, 301 (1904).

(11) Gattermann, *Ber.*, **22**, 1129 (1889).

(12) The analyses were carried out by Miss Theta Spoor and Miss Dorothy Schneider.

(13) *Cf.* Swann and Nelson, *Trans. Electrochem. Soc.*, **67**, 201 (1935); Swann, Univ. Ill. Eng. Expt. Sta. Bull. 236 (1930).

Cleavage of the Pinacolone: 1,1-Dianisylethane.—The pinacolone, 1.5 g., was heated for thirty minutes with 20 g. of potassium hydroxide at 170–180°. The cooled melt was dissolved in 100 cc. of water and the insoluble material collected on a filter. This was recrystallized three times from ethyl alcohol, appearing as fine, white platelets, m. p. 70–72°. A 50-50 mixture of this compound with the original ketone melted around 60°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.47; H, 7.80.

Beckmann Rearrangement: 1,1-Dianisylethene.—A suspension of 0.77 g. of 3,3-dianisyl-2-butanone oxime and 0.2 g. of phosphorus pentachloride in 30 cc. of pure, dry ether was shaken for twenty minutes, or until the oxime had dissolved. When the solution was allowed to stand overnight in the cold it deposited large, clear hexagonal plates. Evaporation and recrystallization yielded 0.47 g. of **1,1-dianisylethene**, m. p. 141–143°.[11]

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.06; H, 6.16.

Summary

Electrolytic reduction of *p*-methoxyacetophenone has been found to produce a mixture of the two possible diastereoisomeric pinacols in excellent yield. These pinacols have been characterized but attempted dehydration to the butadiene has led only to the pinacolone, 3,3-dianisyl-2-butanone.

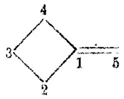
URBANA, ILLINOIS RECEIVED DECEMBER 22, 1943

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 950]

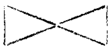
The Structures of Methylenecyclobutane and of 1-Methylcyclobutene

BY W. SHAND, JR., VERNER SCHOMAKER AND J. RODNEY FISCHER

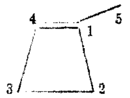
The hydrocarbon prepared by Gustavson[1] by the action of zinc dust on pentaerythrite tetrabromide has been subjected to an intensive chemical investigation[2] on the basis of which structure (I) has been assigned to this substance. The structure may be regarded as definitely established in spite of the appearance of a recent article by Rogowski,[3] who advocated the spiropentane[3a] structure (II) on the basis of electron diffraction studies. A more recent electron diffraction investigation by Bauer and Beach[4] with results in essentially complete disagreement with those of Rogowski is compatible with structure (I) and eliminates structure (II). The hydrocarbon (III) was also first obtained by Gustavson.[5] It is not as readily accessible as (I) and consequently has received less attention from chemists; its structure, however, is not in doubt.[2]



(I)



(II)



(III)

The present investigation was undertaken with the aim of isolating methylenecyclobutane and 1-methylcyclobutene in a state as pure as possible and verifying their structures by the electron diffraction method. It was found, however, that the two compounds cannot readily be distinguished from each other by electron diffraction studies alone, and a determination of only some of the structural details was made, the others being assumed to correspond to the chemically established identity of each compound. The preparation and physical constants of methylenecyclobutane and 1-methylcyclobutene are accordingly described in some detail.

Preparation of Methylenecyclobutane.[6]—Crude pentaerythrityl bromide was made by the procedure in "Organic Syntheses.[7]" Five moles of pentaerythrytol was converted in a single operation to tetrabromide which was washed with water and 95% ethanol[7] and air-dried, average yield 88%. The apparatus used for the hydrocarbon preparation consisted of a 12-liter flask fitted with a three-neck adapter carrying a dropping funnel, mercury-sealed stirrer, and a 38-cm. column without packing equipped with a cold finger at the top and connected to an ice-water cooled condenser; the receiver was surrounded with ice. An intimate mixture of 776 g. (2 moles) of crude tetrabromide and 785 g. (12 moles) of zinc dust was placed in the flask and one liter of water *cautiously* added. The mixture was heated to 85° on a water-bath and 500 cc. of ethanol was added portionwise (*cf.* Philipow, *loc. cit.*) with stirring over a period of two hours or until no more hydrocarbon distilled; frothing was controlled by raising or lowering the stirrer. At the end of the reaction the bath temperature was raised to 95°, forcing over the last traces of hydrocarbon together with some alcohol. The distillate was washed with two 100-cc. portions of water and dried over calcium chloride at 0°, yield 115 g. In a series of runs the yield varied between 70 and 90%. A quantity of the crude hydrocarbon (1340 g.) was twice fractionated through a 22-mm. inside diameter column, 6.5 ft. long, packed with glass helices and fitted with a total reflux, variable take-off

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(1) Gustavson, *J. prakt. Chem.*, [2] **54**, 97 (1896).

(2) More pertinent references: Demjanow, *Ber.*, **41**, 915 (1908); Faworsky and Batalin, *ibid.*, **47**, 1648 (1914); Philipow, *J. prakt. Chem.*, [2] **93**, 162 (1916); Demjanow and Dojarenko, *Ber.*, **55**, 2718, 2727 (1922). The last paper cited demonstrates the identity of the Gustavson hydrocarbon with methylenecyclobutane independently synthesized by a method indicative of structure.

(3) Rogowski, *Ber.*, **72**, 2021 (1939). Structure (II) had previously been advanced in the earlier part of the chemical investigation, but the facts cited in its favor proved on closer examination to be without foundation: Fecht, *Ber.*, **40**, 3883 (1907), *cf.* Mereschkowski, *J. Russ. Phys.-Chem. Soc.*, **46**, 517 (1914) [*Chem. Abst.*, **8**, 3187 (1914); *Chem. Zentr.*, **85**, II, 1266 (1914)]; Zelinsky, *Ber.*, **46**, 160 (1913), *cf.* Philipow, *loc. cit.*, Ingold, *J. Chem. Soc.*, **123**, 1706 (1923).

(3a) A third C_5H_8 hydrocarbon from pentaerythrityl bromide, not identical with either of the Gustavson hydrocarbons discussed in this paper, was recently reported by M. J. Murray and E. H. Stevenson and assigned to formula (II); THIS JOURNAL, **66**, 314 (1944).

(4) S. H. Bauer and J. Y. Beach, THIS JOURNAL, **64**, 1142 (1942).

(5) Gustavson, *J. prakt. Chem.*, [2] **54**, 104 (1896).

(6) The preparations described here were carried out by J. R. F. For details see his Masters' Thesis, California Institute of Technology, 1941.

(7) Schurink in "Organic Syntheses," Vol. **17**, p. 73, J. Wiley, and Sons, Inc., New York, N. Y., 1937.