Copper Bronze.—Ordinary copper bronze sometimes gave very satisfactory and sometimes very poor results in the Ullmann condensation. A simple treatment of the commercial copper bronze made possible more uniform results and frequently made possible a more rapid reaction at a lower temperature.

The copper bronze was treated with a 2% solution of iodine in acetone for about five to ten minutes. This caused it to turn rather grayish in color due to the formation of copper iodide. The product was filtered and treated with dilute hydrochloric acid in acetone. The copper iodide dissolved and the copper bronze remaining was filtered and washed with acetone. It was then dried in a vacuum desiccator. It was found preferable to use this bronze immediately after preparation.

Analysis of Organic Mercury Compounds.—Analyses for mercury were made by a combination of two methods. For the decomposition of the organic mercury compound the method of Tabern[14] was used. The determination of the soluble mercury compound was made through hydrogen sulfide precipitation and weighing of the mercuric sulfide.

Summary

1. 2,2'6,6'-Tetrafluoro-3,3'-dicarboxy-5,5'-dichlorodiphenyl has been prepared. It could not be resolved. The structure of this molecule and of others of a similar character has been discussed.

[14] Tabern and Shelberg, *Ind. Eng. Chem., Anal. Ed.*, **4**, 401 (1932).

URBANA, ILLINOIS

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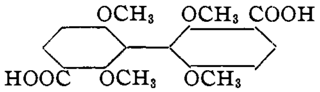
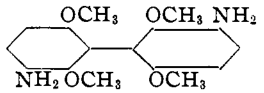
Stereochemistry of Diphenyls. XXXII.[1] Preparation and Properties of Certain 2,2',6,6'-Tetramethoxydiphenyls

BY A. M. VANARENDONK,[2] M. E. CUPERY AND ROGER ADAMS

Simultaneously with the preparation and study of the 2,2',6,6'-tetrafluorodiphenyl described in the previous paper in this series, the synthesis of 2,2',6,6'-tetramethoxydiphenyls has been undertaken. Two compounds 2,2',6,6'-tetramethoxy-3,3'-dicarboxydiphenyl (I) and 2,2',6,6'-tetramethoxy-3,3-diaminodiphenyl (II) have been produced and the properties determined.



I



II

The dicarboxy compound could not be resolved. No mutarotating salts could be obtained even at −17° and no active acid by decomposition of any of the salts.

Resolution of the diamino compound was attempted through the di-

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[1] For the previous paper in this series see Kleiderer and Adams, THIS JOURNAL, **55**, 4219 (1933); see also Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

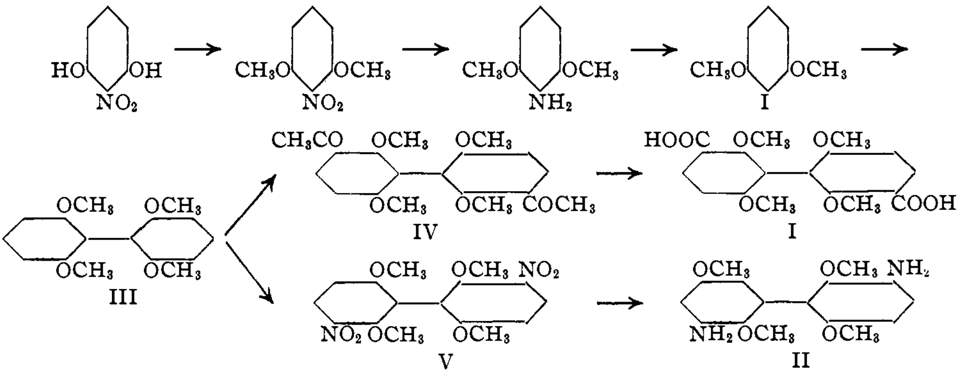
[2] Submitted as part of a thesis for the Degree of Doctor of Philosophy at the University of Illinois.

camphorsulfonate. At 0° the salt showed a rapid mutarotation. On the other hand, if the salt was dissolved as quickly as possible in methyl alcohol at −17° and the rotation determined at that temperature, readings of the mutarotation could readily be recorded. Although necessarily qualitative in character, several repetitions of the experiment gave the same results. It would appear, then, that four methoxyl groups represent about the lower limit for obtaining restricted rotation in the diphenyl molecules at temperatures above −17°. On the basis of calculations previously used for relative interference values, the internuclear distance from the carbon of the ring to the center of the methoxyl group is approximately 1.45 Å. A similar conclusion may be drawn from the results of this investigation.

By comparing the racemization rates of 2,2′-difluoro-6,6′-dicarboxydiphenyl;[3] 2,2′-difluoro-6,6′-diamino-3,5,3′,5′-tetramethyldiphenyl;[4] 2-nitro-6-carboxy-2′-methoxydiphenyl;[5] 2-nitro-6-carboxy-2′-fluorodiphenyl[5] and 2,2′-dimethoxy-6,6′-dicarboxydiphenyl[3,6] it may be concluded that the methoxyl group is substantially larger than the fluorine and substantially smaller than the amino group so far as concerns interference effects in the diphenyl molecules.

Experimental

The two compounds studied were produced by the following series of reactions.



2-Iodo-1,3-resorcinol Dimethyl Ether.—This compound has been previously described[7] but modifications in the various steps as used in this investigation will be outlined briefly.

(A) **2-Nitro-1,3-resorcinol.**—Resorcinol was nitrated as described by Kaufmann and de Pay[8] except that it was first dissolved in cold concentrated sulfuric acid.

(B) **2-Nitro-1,3-resorcinol Dimethyl Ether.**—A solution of 50 g. of dry 2-nitroresorcinol in 300 cc. of dry toluene was heated to boiling and 80 cc. of dimethyl sulfate

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(3) Stanley, McMahon and Adams, This Journal, **55**, 706 (1933).

(4) Kleiderer and Adams, *ibid.*, **53**, 1575 (1931).

(5) Stoughton and Adams, *ibid.*, **54**, 4426 (1932).

(6) Kenner and Turner, *J. Chem. Soc.*, 2340 (1928).

(7) Kaufmann and Franck, *Ber.*, **40**, 4014 (1907); Baeyer, *Ann.*, **372**, 127 (1910).

(8) Kaufmann and de Pay, *Ber.*, **37**, 726 (1904).

added. At about 100° with stirring 100 g. of finely powdered anhydrous potassium bicarbonate was added in small amounts sufficient to produce a brisk evolution of carbon dioxide. After fifteen minutes about 2 cc. of water was carefully added with the solution temperature at 100°. The stirring was continued for one hour with the temperature at 90–100°. Another 15 cc. of dimethyl sulfate was added with another small amount of water, and the heating continued until the solid material in the flask became nearly white (fifteen to thirty minutes). At this point 5 g. of powdered sodium carbonate was added to destroy any excess of dimethyl sulfate, and stirring and heating continued for about fifteen minutes. The hot solution was filtered, the toluene removed by distillation under reduced pressure and the solid residue dissolved in 150 cc. of hot butyl alcohol. After treatment with norite, 2-nitro-1,3-resorcinol dimethyl ether separated upon cooling. Another butyl alcohol–norite treatment followed by crystallization from 80% alcohol gave white crystals, m. p. 130°, yield 83%.

(C) **2-Amino-1,3-resorcinol Dimethyl Ether.**—The nitro compound was reduced catalytically[9] in alcohol with platinum oxide and hydrogen at a pressure of 2–3 atm.; yield quantitative.

(D) **2-Iodo-1,3-resorcinol Dimethyl Ether.**—The iodo compound was made as described by Kaufmann and Franck[10] except that the amine was dissolved in 95% acetic acid containing excess over the theoretical of concentrated sulfuric acid; m. p. 102–103°; yield 85%.

2,2',6,6'-Tetramethoxydiphenyl (III).—A mixture of 15 g. of pure powdered 2-iodo-1,3-resorcinol dimethyl ether and 45 g. of very finely divided copper bronze was tightly packed into a large Pyrex test-tube and covered with a layer of copper bronze. A closely fitting cork stopper was then inserted into the tube directly above the reaction mixture. The tube was heated in an oil-bath, the temperature of which was 170–200° for two to three hours and finally 210° for fifteen minutes. After cooling, the reaction mixture was extracted in a Soxhlet apparatus with acetone for twenty hours. The tetramethoxydiphenyl crystallized from the acetone on cooling. The 2,2',6,6'-tetramethoxydiphenyl is easily purified by recrystallization from acetone containing a little water; m. p. 175–176°, yield 6–7 g. (85–90%).

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.03; H, 6.62. Found: C, 69.76; H, 6.78.

The tetramethoxydiphenyl was also prepared by means of the Grignard reaction, by treatment with anhydrous cupric chloride. The yield was much lower than in the Ullmann reaction, but the compound proved to be identical in every way.

2,2',6,6'-Tetramethoxy-3,3'-diacetodiphenyl (IV).—A mixture of 5 g. of pure tetramethoxydiphenyl, 75 cc. of dry carbon disulfide and 25 cc. of acetyl chloride was placed in a 3-necked flask with a mechanical stirrer and a thermometer. After cooling by means of an ice-bath, 5 g. of anhydrous ferric chloride was added with vigorous stirring followed in a few minutes by another equal amount. Stirring was continued vigorously for fifteen to twenty minutes. The flask was allowed to warm gradually to about 30° and stirring was continued for about half an hour, until a brown pasty mass settled to the bottom of the flask. The carbon disulfide solution was decanted and discarded. The residue was added to warm water, then well cooled and filtered. The solid was dissolved in a small quantity of alcohol and the colloidal ferric chloride removed by adding a small portion of sodium hydroxide and filtering.

The product can be crystallized from dilute alcohol but it is necessary to allow the solution to stand in a refrigerator for several days. If the alcohol is too dilute the diaceto compound may separate as an oil and may also be recrystallized from an ethyl acetate solution to which an equal volume of petroleum ether has been added. The pure com-

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(9) "Organic Syntheses," Coll. Vol. I, (1932), pp. 53, 235, 452.

(10) Kaufmann and Franck, *Ber.*, **39**, 2724 1906.

pound is perfectly white and has m. p. 113–115°. The yields in this preparation varied widely and detailed directions were not discovered that would assure constant results.

As the diaceto derivative is not very easily purified by crystallization it was generally oxidized in a crude state.

Anal. Calcd. for $C_{20}H_{22}O_6$: C, 67.01; H, 6.19. Found: C, 67.15; H, 6.34.

2,2',6,6'-Tetramethoxy-3,3'-dicarboxydiphenyl (I).—The crude diaceto compound was oxidized as described by Cupery and VanArendonk.[11] From 5 g. of diaceto compound, 75 cc. of methanol, 15 cc. of 20% sodium hydroxide solution and excess hypochlorite, there was obtained 2 g. of dibasic acid.

The 2,2',6,6'-tetramethoxy-3,3'-dicarboxydiphenyl has one molecule of water of crystallization. It may be further purified by drying in an oven at 110° overnight, and then recrystallizing it from absolute ethyl acetate. It crystallized with one molecule of ethyl acetate, which was removed by heating in an oven at 125° for several hours, m. p. 231–232°.

Anal. Calcd. for $C_{18}H_{18}O_8 \cdot H_2O$: H_2O, 4.74. Found: H_2O, 4.89. Calcd. for $C_{18}H_{18}O_8 \cdot CH_3CO_2C_2H_5$: $CH_3CO_2C_2H_5$, 19.56. Found: $CH_3CO_2C_2H_5$, 19.76. Calcd. for $C_{18}H_{18}O_8$: neut. equiv., 362; C, 59.64; H, 5.01. Found: neut. equiv., 367; C, 59.56; H, 5.34.

Attempted Resolution of I

Salt	Weight	Made up to in chloroform, cc.	$l = 2$ α_D	$[\alpha]^{20}_D$
Brucine	0.1500	15	−0.36°	− 18°
Strychnine	.1500	15	−1.04	− 52
Cinchonine	.0500	10	+1.08	+108

All salts were very soluble in water and in many organic solvents. The free acid was difficult to obtain from the salts since in acid solution the free acid loses carbon dioxide on heating. The brucine salt was prepared in absolute ethanol from anhydrous brucine and anhydrous acid and fractionally precipitated by adding carbon tetrachloride. It may be recrystallized from a 1:2 mixture of pyridine and carbon tetrachloride. The strychnine and cinchonine salts were formed in alcohol solution, the solution evaporated to dryness and treated with ethyl acetate. All salts gave fractions with the same rotation, showed no mutarotation and gave inactive acids on decomposition.

2,2',6,6'-Tetramethoxy-3,3'-dichloro-5,5'-dicarboxydiphenyl.—Into a solution of 1 g. of tetramethoxydiacetodiphenyl and a small quantity of iodine in 25 cc. of glacial acetic acid chlorine was slowly passed for several hours. The mixture was then slowly poured into cold aqueous sodium bisulfite. A heavy precipitate formed which was filtered. On warming to room temperature the substance became very sticky and no method was discovered for purification. It was, therefore, oxidized directly to the dibasic acid according to the method of Cupery and VanArendonk.[11]

The crude product was dried in an oven at 105° and gave a hard brown mass. This was dissolved in anhydrous ethyl acetate and filtered. Upon adding three volumes of petroleum ether, and allowing to stand in a cool place overnight, white crystals formed, m. p. 202–203°. A portion was recrystallized from ethyl acetate and petroleum ether and gave the same melting point.

Anal. Calcd. for $C_{18}H_{16}O_8Cl_2$: neut. equiv., 433; Cl, 16.6. Found: neut. equiv., 438; Cl, 17.1.

2,2',6,6'-Tetramethoxy-3,3'-dinitrodiphenyl (V).—To 1 g. of 2,2',6,6'-tetramethoxydiphenyl was added a mixture of 10 cc. of acetic anhydride and 0.6 cc. of concentrated nitric acid. The latter was prepared by warming fuming nitric acid (sp. gr. 1.5) until

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(11) Cupery and VanArendonk, This Journal, **53**, 3184 (1931).

colorless. The mixture was heated until the reaction started, which was evidenced by a violent boiling, and a slight evolution of nitrogen dioxide fumes. When the boiling had ceased, the solution was heated on a hot-plate to incipient boiling for five minutes and was then allowed to stand for four hours at room temperature. An equal volume of water was added, and the mixture was heated slightly to decompose the acetic anhydride. Upon cooling the solution, an orange-colored precipitate was obtained which weighed 1 g. This was recrystallized several times from a minimum amount of hot alcohol and acetone mixture (1:1) with norite; white crystals, m. p. 174°; yield 0.7 g.

Anal. Calcd. for $C_{16}H_{16}O_8N_2$: C, 52.75; H, 4.40; N, 7.69. Found: (micro) C, 52.93; H, 4.52; N, 7.64.

2,2',6,6'-Tetramethoxy-3,3'-diaminodiphenyl (II).—A mixture of 3 g. of carefully purified 2,2',6,6'-tetramethoxy-3,3'-dinitrodiphenyl in 150 cc. of alcohol was heated to 50° and reduced with platinum oxide catalyst and hydrogen at 40 lb. pressure. The solution after filtration of the catalyst was evaporated under reduced pressure to 20 cc. and cooled in an ice-bath, whereupon practically all of the diamino compound precipitated. The diamine was recrystallized twice from hot alcohol to a perfectly white compound, m. p. 159–160°. Upon standing exposed to the air, the compound colored slightly, but this did not affect the melting point; yield, 2.3 g. (95%).

Anal. Calcd. for $C_{16}H_{20}O_4N_2$: C, 63.16; H, 6.58; N, 9.21. Found: (micro) C, 63.36; H, 6.62; N, 9.45.

Attempted Resolution of 2,2',6,6'-Tetramethoxy-3,3'-diaminodiphenyl.—A solution of 1.1 g. of the diphenyl in 40 cc. of acetone was added to 1.5 g. of *d*-camphorsulfonic acid in 70 cc. of acetone. The solution was heated to boiling for one-half minute and allowed to cool to room temperature and to evaporate slowly. After three days, 0.2 g. of fine crystals was obtained. These were very dark brown in color, and the rotation could not be determined. On further standing, 0.8 g. of fine, white, powdery crystals separated, which softened at 220° and melted at 229–232° (uncorr.).

Anal. Calcd. for $C_{36}H_{52}O_{12}N_2S_2$: C, 56.25; H, 6.79; N, 3.65. Found: (micro) C, 56.40; H, 6.99; N, 3.71.

Mutarotation was so rapid that no very accurate values could be obtained at 0°. By working rapidly at $-17°$ the initial reading could be taken in one and one-half minutes. Several determinations showed mutarotation in each instance though the results were too qualitative to warrant determination of the half life period.

Rotation. 0.04 g. of substance made up to 10 cc. in methanol gave at $-17°$ α_D $+0.34$, $l = 1$; $[\alpha]^{-17}_D$ $+85°$; in less than two minutes α_D $+0.13$, $l = 1$; $[\alpha]^{-17}_D$ $+32.5$ which remained constant.

2,2',6,6'-Tetraacetoxydiphenyl.—A solution of 2 g. of tetramethoxydiphenyl in 100 g. of glacial acetic acid and 8 g. of 40% hydrobromic acid was refluxed for nine hours and then allowed to stand overnight. Upon concentration to 3–4 cc. under reduced pressure, a thick viscous liquid remained which could not be crystallized. About 15 cc. of acetic anhydride was added and this solution kept just below boiling temperature for one hour. After cooling, water was added and the white solid obtained was purified by recrystallization from alcohol as white needles, m. p. 190°.

Anal. Calcd. for $C_{20}H_{18}O_8$: C, 62.15; H, 4.69. Found: C, 62.15; H, 5.01.

2,2',6,6'-Tetramethoxy-3,3',5,5'-tetranitrodiphenyl.—One gram of tetramethoxydiphenyl was gradually added with stirring to 20 g. of fuming nitric acid at 0°. Upon standing for two hours, the colored solution cleared to a pale yellow and was then poured into cold water. The product after several recrystallizations from acetic acid formed needle crystals, m. p. 194–195°.

Anal. Calcd. for $C_{16}H_{14}O_{12}N_4$: C, 42.09; H, 3.53. Found: C, 42.25; H, 3.38.

2,2′,6,6′-Tetramethoxy-3,3′,5,5′-tetraacetodiphenyl.—To a solution of 2 g. of tetramethoxydiphenyl in 30 cc. of hot acetic anhydride was added 4 g. of anhydrous aluminum bromide. The solution was gently refluxed for two hours and about 50 cc. of alcohol then added through the condenser. The solution was concentrated to about 30 cc., an equal volume of alcohol was added and the warm solution filtered. The white solid residue was dissolved in hot 10% sodium hydroxide, filtered, and reprecipitated with acetic acid. It was purified from glacial acetic acid, white crystals, m. p. with dec. 340–350°.

Anal. Calcd. for $C_{24}H_{26}O_8$: C, 65.13; H, 5.92. Found: C, 65.15; H, 5.64.

Summary

2,2′,6,6′-Tetramethoxy-3,3′-dicarboxydiphenyl and 2,2′,6,6′-tetramethoxy-3,3′-diaminodiphenyl have been prepared. The former could not be resolved and no mutarotation of the salts was observed. The latter gave a dicamphorsulfonate that mutarotated at −17°.

Urbana, Illinois

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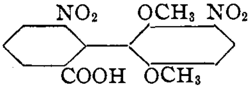
[Contribution from the Chemical Laboratory of the University of Illinois]

Stereochemistry of Diphenyls. XXXIII.[1] Preparation and Properties of 2,3′-Dinitro-6-carboxy-2′,6′-dimethoxydiphenyl and 2-Nitro-6-carboxy-2′-fluoro-6′-methoxydiphenyl

By A. M. VanArendonk,[2] B. C. Becker and Roger Adams

In previous papers a description of the properties of 2,2′,6,6′-tetrafluoro-3,3′-dichloro-5,5′-dicarboxydiphenyl;[3] 2,2′,6,6′-tetramethoxy-3,3′-dicarboxydiphenyl;[1] 2,2′,6,6′-tetramethoxy-3,3′-diaminodiphenyl;[1] and 2,2′-difluoro-6,6′-dimethoxy-3,3′-dicarboxydiphenyl[4] has been given. None of these compounds could be resolved and only in the case of the 2,2′,6,6′-tetramethoxy-3,3′-diaminodiphenyl was it possible to observe the mutarotation of a salt at a temperature of −17°.

In this investigation two compounds have been prepared in which the 2,6 substituents were represented, respectively, by one fluorine and one methoxyl and by two methoxyls, while the 2′,6′ groups were nitro and carboxyl. The specific compounds were 2,3′-dinitro-6-carboxy-2′,6′-dimethoxydiphenyl (I) and 2-nitro-6-carboxy-2′-fluoro-6′-methoxydiphenyl (II).



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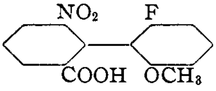

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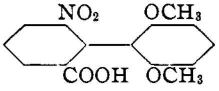

III

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[1] For previous papers in the series see VanArendonk, Cupery and Adams, This Journal, **55**, 4225 (1933). See also Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

[2] Submitted as part of a thesis for the Degree of Doctor of Philosophy at the University of Illinois.

[3] Kleiderer and Adams, This Journal, **55**, 4219 (1933).

[4] Becker and Adams, *ibid.*, **54**, 2973 (1932).