Reduction of Anisalchlorimine to *o*-Methoxybenzylamine.—Two grams of the chlorimine in alcoholic solution was reduced with sodium amalgam at about 30° by the method described in a recent paper.[1] A 64% yield of white crystals of amine hydrochloride was obtained.

Anal. Calcd. for $C_8H_{11}ON \cdot HCl$: N, 8.05. Found: N, 8.04.

Summary

o-Chlorobenzalchlorimine and anisalchlorimine were prepared from the corresponding aldehyde and monochloramine. Since the former chlorimine is more stable than the latter, chlorine in the ortho position apparently has a greater influence on the stability of the chlorimine than has the methoxy group in the para position.

The chlorimines decompose slowly at room temperatures and more rapidly as the temperature is raised into hydrogen chloride and the corresponding nitrile.

DURHAM, NORTH CAROLINA

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

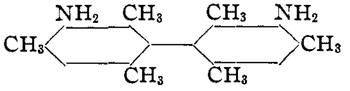
STEREOCHEMISTRY OF DIPHENYL COMPOUNDS. V. PREPARATION AND RESOLUTION OF 2,4,6,2′,4′,6′-HEXANITRO-3,3′-DICARBOXYDIPHENYL[1]

BY L. H. BOCK,[2] W. W. MOYER[2] AND ROGER ADAMS

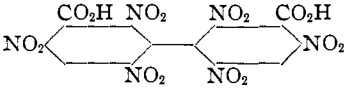
RECEIVED JANUARY 20, 1930 PUBLISHED MAY 8, 1930

The resolution of 2,4,6,2′,4′,6′-hexamethyl-3,3′-diaminodiphenyl (I)[1b] (diaminodimesityl) demonstrated that the groups in the 2,6,2′,6′-positions in diphenyl could all be methyl and still render the molecule capable of existing in optically active forms. The conclusion from this research was that probably any group in place of the methyl would be equally satisfactory for producing similar results providing it is sufficiently large.

In this investigation the preparation of a compound containing four nitro groups in the 2,2′,6,6′-positions was undertaken and the specific compound studied was 2,4,6,2′,4′,6′-hexanitro-3,3′-dicarboxydiphenyl (II).



I



II

This substance is of particular interest as compared to diaminodimesityl because of the entirely different electrochemical character of the nitro

---

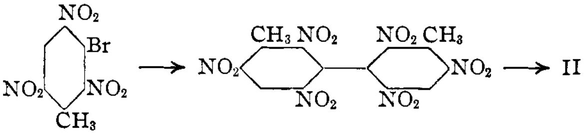
[1] Previous papers in this field are: (a) Hyde and Adams, THIS JOURNAL, **50**, 2499 (1928); (b) Moyer and Adams, *ibid.*, **51**, 630 (1929); (c) Stanley and Adams, *Rec. trav. chim.*, **48**, 1035 (1929); (d) THIS JOURNAL, **52**, 1200 (1930).

[2] This communication is an abstract of portions of theses submitted by W. W. Moyer and L. H. Bock in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

and methyl groups, due chiefly to the extra unshared electrons in the former. It was found that this compound could be readily resolved through the strychnine salt.

The optically active isomers were resistant to racemization. Ten hours of refluxing in glacial acetic acid or twelve hours of heating at 90–95° in 5% ammonium carbonate solution resulted in essentially no change in rotation. A cold 5% solution of sodium bicarbonate had no effect and heating in the same solution for one and one-half hours at 100° changed the rotation only about 4%. Since this latter treatment caused a coloring of the solution, it is likely that decomposition may have accounted for the slight change. The x-ray data presented in the previous paper would lead to the expectation that the optically active 2,2′,6,6′-tetranitro-3,3′-dicarboxydiphenyl would have no tendency to racemize.

The 2,4,6,2′,4′,6′-hexanitro-3,3′-dicarboxydiphenyl was prepared by nitration of 3-bromotoluene to the trisubstituted derivative (III), condensation of this to 2,4,6,2′,4′,6′-hexanitro-3,3′-dimethyldiphenyl (IV) and oxidation of the methyl groups to the dibasic acid (II).



III IV

The condensation of trinitrobromotoluene to the diphenyl derivative by means of copper was accomplished only after very carefully regulated conditions were discovered. Successful results were obtained with nitrobenzene as a solvent and a temperature about 10° below the point where trinitrobromotoluene and copper give a vigorous exothermic reaction. The oxidation of the condensation product took place readily with a mixture of sodium dichromate, sulfuric acid and fuming nitric acid. The final acid showed no signs of resolution with brucine or quinine but readily separated into two salts with strychnine. Hexanitrodicarboxydiphenyl did not lose carbon dioxide readily, as after heating in various solvents there were no signs of decomposition.

A few words concerning the unsuccessful experiments to obtain 2,4,6,2′,4′,6′-hexanitro-3,3′-dimethyldiphenyl and other compounds with the 2,6,2′,6′-position filled with nitro groups should be included. (1) 3,3′-Dimethyldiphenyl, which was readily prepared by the action of 3-tolylmagnesium bromide with cupric chloride could, in spite of many experiments, be nitrated only to the tetranitro compound with only two of the nitro groups undoubtedly in the desired positions. (2) From tolidine by tetrazotization and treatment with cuprous cyanide, 3,3′-dimethyl-4,4′-dicyanodiphenyl was obtained which was then hydrolyzed to 3,3'-dimethyl-4,4'-dicarboxydiphenyl. Nitration gave what at first appeared to be the desired 2,6,2',6'-tetranitro compound. A few attempts at resolution failed but no exhaustive study was made owing to the uncertainty of the constitution of the product. (3) Through the 4-chloro derivative of *o*-acetoluidide by hydrolysis, diazotization, introduction of the cyano group and hydrolysis, 4-chloro-2-methylbenzoic acid was obtained. Contrary to the reports in the literature, no dinitro compound could be obtained which it was hoped might be esterified and condensed with copper to the diphenyl derivative, 2,6,2',6'-tetranitro-4,4'-dicarboxy-3,3'-dimethyldiphenyl.

Experimental

2,4,6-Trinitro-3-bromotoluene.—The preparation was carried out in two steps. Dinitro-3-bromotoluene was prepared first as suggested by Grete[3] by the nitration of 3-bromotoluene and then further nitrated to the trinitro compound by the method of Bentley and Warren.[4]

2,4,6,2',4',6'-Hexanitro-3,3'-dimethyldiphenyl.—In a 500-cc. three-necked flask fitted with a thermometer and a mechanical stirrer was placed a solution of 110 g. of trinitrobromotoluene in 320 cc. of nitrobenzene. The flask was heated on an oil-bath to 160°, at which point about 5 g. of copper powder (Kahlbaum's Naturkupfer C) was added and the temperature slowly raised to 175° with constant stirring. At this temperature the reaction begins to take place as evidenced by the loss of metallic luster of the copper and a rise in temperature. The flame under the oil-bath was turned low and the temperature was maintained at 175–183° by adding copper powder slowly until 110 g. in all had been used. A higher temperature than 183° must be avoided since this results in a tarry product difficult to purify. The mixture was stirred for one-half hour at 175–180° after all the copper powder was added. The flask was then allowed to cool and the copper residue was filtered off and washed with acetone. The filtrate and washings were combined and subjected to steam distillation to remove all the nitrobenzene. The product was filtered from the water in the flask, dissolved in about one liter of acetone and refluxed for an hour with 25 g. of norite. The norite was filtered off and the acetone was removed by distillation until the volume was about 100 cc. When allowed to stand for several hours the hexanitromethyldiphenyl crystallized in yellow granular crystals. The product was recrystallized from glacial acetic acid. Fifty-seven grams (70%) of a light yellow product melting at 240–241° was obtained. Hexanitrodimethyl diphenyl is practically insoluble in alcohol and ether but very soluble in acetone. It dissolves in warm benzene, toluene and acetic acid.

Anal. Calcd. for $C_{14}H_8O_{12}N_6$: H, 1.78; C, 37.16. Found: H, 1.87, 1.90; C, 36.72, 37.1.

2,4,6,2',4',6'-Hexanitro-3,3'-dicarboxydiphenyl.—A solution was made of 33 g. of hexanitrodimethyldiphenyl in a mixture of 330 cc. of fuming nitric acid (1.52 sp. gr.; moreover, the acid must be of superior grade to give good results) and 115 cc. of 20% fuming sulfuric acid. The solution was placed in a one-liter three-necked flask equipped with a thermometer and a mechanical stirrer. The mixture was cooled to 20° with stirring and 120 g. of sodium dichromate was added slowly over a period of one-half hour. The temperature was maintained below 30°. The temperature rises very slowly and the reaction requires attention for two hours or more in order to maintain the

---

[3] Grete, *Ann.*, **177**, 258 (1875).

[4] Bentley and Warren, *Am. Chem. J.*, **12**, 4 (1890).

proper temperature. The mixture was stirred for twenty hours at room temperature and poured into one kilo of cracked ice. A white powdery precipitate was formed which was filtered off and washed with 20% hydrochloric acid. The solid was dissolved in 250 cc. of cold alcohol and filtered to remove any insoluble unreacted material. The filtrate was treated with concentrated hydrochloric acid to reprecipitate the hexanitrodicarboxydiphenyl. This was filtered and recrystallized from one liter of benzene. A yield of 27 g. (72%) of pure acid was obtained, melting at 292–293°. Hexanitrodicarboxydiphenyl is colorless when pure but rapidly turns yellow when allowed to stand in the air. For this reason it was always dried in a vacuum desiccator. It is very soluble in acetone, alcohol and ether, and warm water. It dissolves slowly in boiling benzene and separates as long colorless needles on cooling.

Anal. Calcd. for $C_{14}H_4O_{16}N_6$: N, 16.41. Found: N, 16.14, 16.57.

Resolution of 2,4,6,2′,4′,6′-Hexanitro-3,3′-dicarboxydiphenyl.—A solution of 10 g. of hexanitrodicarboxydiphenyl was dissolved in 500 cc. of methyl alcohol and added to 13.5 g. of strychnine dissolved in 3 liters of methyl alcohol. The solution was allowed to stand for several hours and the salt was filtered off. Concentration of the mother liquor showed that practically all of the salt had separated. The salt was dissolved in a mixture of one-third pyridine and two-thirds water by volume and crystallized slowly. The first fractions were recrystallized three times from the same solvent to obtain the maximum levo rotation. The soluble fraction separated as a gum on concentrating the mother liquors. By adding acetone to these mother liquors, the gum crystallized. Two recrystallizations yielded a salt of constant dextro rotation. The yields obtained were about 6 g. of *l*-salt and 4 g. of *d*-salt.

l-Salt. 0.1080 made up to 15 cc. with pyridine at 20° gave α_D − 0.54; $l = 1$, $[\alpha]^{20}_{D}$ −74.7°.

d-Salt. 0.1171 made up to 15 cc. with pyridine at 20° gave α_D 0.47, $l = 1$, $[\alpha]^{20}_{D}$ +60.0°.

No sharp melting point could be obtained for either salt as they decomposed above 250°, the *l*-salt decomposing at a slightly higher temperature.

Anal. Calcd. for $C_{66}H_{48}O_{20}N_{10}$: H, 4.1, C, 56.93. Found: *l*-salt—H, 4.0; C, 57.4. *d*-salt—H, 4.2; C, 58.04.

It was found impossible to resolve this compound either by means of brucine or quinine. Attempts to resolve by adding portions of strychnine to the acid and fractionally precipitating salt in this way gave variable results due, probably, to the separation of both normal and acid salt in the fractions.

***d*- and *l*-2,4,6,2′,4′,6′-Hexanitro-3,3′-dicarboxydiphenyls.**—The active acids were liberated from the active salts by treating with hydrochloric acid in alcohol. To a mixture of 150 cc. of 95% alcohol and 40 cc. of concentrated hydrochloric acid was added 4.5 g. of *l*-salt. The mixture was placed in a 500-cc. round-bottomed flask and stirred at 60° for two hours. The mixture was then cooled and 50 cc. of concentrated hydrochloric acid was added to insure the complete precipitation of the free acid. The mixture was then cooled to 0° and filtered. The solid obtained was redissolved in 95% alcohol, filtered to remove any undecomposed salt and again precipitated with hydrochloric acid. A yield of 2 g. of acid was obtained. The acid was recrystallized by dissolving in acetone and concentrating until crystals started to separate. An equal volume of benzene was then added and the solution allowed to stand until the acid had all crystallized. A pure acid was then readily obtained but the recovery was very poor. The product melts with decomposition at about 230–240°.

l-acid: 0.1143 g. made up to 15 cc. with acetone at 20° gave α_D −0.17°, $l = 1$, $[\alpha]^{20}_{D}$ −21.84°. 0.2230 g. made up to 25 cc. with acetic acid at 20° gave α_D −0.24°, $l = 1$, $[\alpha]^{20}_{D}$ −27.22°. 0.1034 g. made up to 15 cc. with 5% $NaHCO_3$ solution at 20°

gave α_D $-0.55°$, $l = 1$, $[\alpha]_D^{20}$ $-80.5°$. 0.1377 g. made up to 25 cc. with 5% $(NH_4)_2CO_3$ solution at 20° gave α_D $-0.37°$, $l = 1$, $[\alpha]_D^{20}$ $-66.74°$.

The *d*-acid was obtained from the *d*-salt by similar treatment. To a mixture of 15 cc. of 95% alcohol and 5 cc. of concentrated hydrochloric acid was added 0.6 g. of *d*-salt. On stirring, the salt completely dissolved, showing that it decomposed readily in the cold. An additional 5 cc. of concentrated hydrochloric acid was added to precipitate the free acid, and it was purified by the same method as used with the *l*-acid. About 0.2 g. of *d*-acid was obtained.

d-Acid. 0.0555 g. made up to 15 cc. with 5% $NaHCO_3$ solution at 20° gave α_D $+0.29°$, $l = 1$, $[\alpha]_D^{20}$ $+79.67°$.

Racemization Experiments on Active Acids

1. A solution of 0.223 g. of *l*-acid in 25 cc. of glacial acetic acid was prepared and the initial specific rotation was $[\alpha]_D^{20}$ $-27.22°$. The solution was heated for four hours at 100° in a flask connected with a reflux condenser by a ground-glass connection. The solution showed no change in rotation. The solution was then refluxed for ten hours, when it showed a slightly increased rotation which was probably caused by the concentration of the acetic acid through loss from the top of the condenser. The acid was precipitated by adding an equal volume of concentrated hydrochloric acid. The acid so precipitated was filtered and dried in a vacuum desiccator and the rotation determined.

0.0528 g. made up to 15 cc. with 5% $NaHCO_3$ solution at 20° gave α_D $- 0.26°$, $l = 1$, $[\alpha]_D^{20}$ $-73.89°$.

2. A 5% sodium bicarbonate solution was made and rotations were read at intervals for three days during which time the solution was stored in a dark place at room temperature.

Initial Rotation.—0.1034 g. made up to 15 cc. with 5% $NaHCO_3$ solution at 20° gave α_D $-0.55°$, $l = 1$, $[\alpha]_D^{20}$ $-80.5°$. *Rotation after eighty hours.*—α_D $-0.53°$, $l = 1$, $[\alpha]_D^{20}$ $-76.5°$.

3. A sodium bicarbonate solution was heated on a steam-bath for one and one-half hours. At the end of this time it was becoming colored so the heating was not continued. The solution was not made up to standard volume but the rotation changed from an initial reading of α_D $-0.28°$ to a final reading of α_D $-0.26°$. The changing of color may have affected the rotation here as in the experiment described above. Sodium carbonate solution could not be used as it became deep red on short standing.

4. A sample of *l*-acid was heated in a 5% ammonium carbonate solution for twelve hours on a water-bath at 85–95°. The solution did not become colored.

Initial rotation.—0.1377 g. made up to 25 cc. with 5% $(NH_4)_2CO_3$ solution at 25° gave α_D $-0.37°$, $l = 1$, $[\alpha]_D^{20}$ $-66.74°$. *Rotation after twelve hours of heating.*—α_D $-0.35°$; $l = 1$, $[\alpha]_D^{20}$ $-62.96°$.

3,3′-Dimethyldiphenyl.—A Grignard solution was prepared from 342 g. of pure 3-bromotoluene and 49 g. of magnesium turnings in 750 cc. of dry ether and a few crystals of iodine. A suspension of 300 g. of finely powdered anhydrous cupric chloride in 600 g. of ether was added with stirring while the flask was cooled with ice. The mixture was refluxed overnight. Decomposition by pouring on ice and hydrochloric acid yielded 3,3′-dimethyldiphenyl, which distilled at 138–139° at 5 mm. The yield was 118 g. (64%).

Tetranitro-3,3′-dimethyldiphenyl.—To 50 g. of fuming nitric acid cooled to −5° was added slowly, with vigorous stirring, 10 g. of 3,3′-dimethyldiphenyl. The temperature was not allowed to rise above 0° during the whole addition. Then, with stirring, 50 g. of concentrated sulfuric acid was added and the temperature allowed to go up to 60–70°. The mixture was stirred for two hours and then poured on cracked ice. The white product was filtered, washed, dried and recrystallized from 250 cc. of glacial acetic acid until pure. Nine g. of light-yellow crystals of a constant melting point at 234° (corr.) was obtained.

Anal. Calcd. for $C_{14}H_{10}O_6N_4$: C, 46.40; H, 2.78. Found: C, 46.78; H, 2.87.

The acetic acid filtrate from the first recrystallization, upon dilution with water, gave a gummy material, which was recrystallized many times from alcohol. Finally, a substance melting over the range 102–110° was obtained which was not identified.

All attempts at further nitration by heating with fuming nitric and fuming sulfuric acids under varying conditions were unsuccessful.

3,3′-Dimethyl-4,4′-dicarboxydiphenyl.—A solution of 210 g. of concentrated sulfuric acid and 140 g. of water was heated to 160° in a 2-liter, three-necked flask fitted with stirrer, thermometer and reflux condenser. 3,3′-Dimethyl-4,4′-dicyanodiphenyl[5] was added, with vigorous stirring, in small amounts to the hot acid solution. A deep purple color at first appeared, but faded with the separation of a grayish solid. Hydrolysis was continued for five hours at 150–160°, with constant stirring. The reaction mixture was poured into ice water and filtered. The acidic product was dissolved in dilute alkali solution and decolorized with norite. By the addition of hydrochloric acid, the product came down as a gelatinous mass that could not be filtered dry by suction. The wet acid was dried in a vacuum oven at 120°. The weight of crude acid was 71 g., the extra weight over the calcd. 64 g. being due to the inorganic salt occluded in the gelatinous mass. The compound was not further purified, but pulverized, and used in the nitration as such.

Nitration of 3,3′-Dimethyl-4,4′-dicarboxydiphenyl.—In a 1-liter, three-necked flask fitted with a thermometer and mechanical stirrer, was placed 300 g. of fuming nitric acid. The flask was surrounded by an ice–salt freezing mixture and the nitric acid cooled to −5°. Then, with stirring, the 71 g. of crude 3,3′-dimethyl-4,4′-dicarboxydiphenyl described in the last preparation was added in small amounts, while the temperature was kept at 0° or below. Then, through a separatory funnel was added 700 g. of 15% fuming sulfuric acid. The temperature rose to 65°, at which point a solid began to separate from the solution, with foaming. The mixture was stirred for an hour at 65° and then heated to 90° for one-half hour. The cool nitration mixture was poured on cracked ice and the product filtered. The crude product was dissolved in dilute ammonium hydroxide solution and reprecipitated with hydrochloric acid. After filtering and washing the weight was 78 g.

The nitro compound was then decolorized by boiling with norite in 600 cc. of alcohol. The alcohol filtrate from the norite was heated to boiling and hot water was added until turbidity was noticed. On cooling, 40 g. of yellowish-white crystals, powder-like in fineness, were obtained. The melting point was 320–350° with decomposition.

Anal. Neut. equiv. Subs., 0.2070 g. required 12.0 cc. of 0.0733 *N* alkali. Calcd. mol. wt.: 225. Found: 235.

After four crystallizations from dilute alcohol, a product with a neutral equivalent of 227 was obtained. The melting point range was 330–350° due to decomposition dependent upon the rate of heating.

Anal. Calcd. for $C_{16}H_{10}O_{12}N_4$: C, 42.66; H, 2.24. Found: C, 42.66; H, 2.29.

Summary

1. 2,4,6,2′,4′,6′-Hexanitro-3,3′-dicarboxydiphenyl has been prepared by condensing 2,4,6-trinitro-3-bromotoluene with copper and oxidizing the resulting 2,4,6,2′,4′,6′-hexanitro-3,3′-dimethyldiphenyl with a mixture of fuming nitric acid, sulfuric acid and sodium dichromate.

---

[5] Löwenherz, *Ber.*, **25**, 1036 (1892).

2. The compound was readily resolved through the strychnine salt.
3. The active forms did not racemize under the ordinary conditions which might be expected to effect racemization.

URBANA, ILLINOIS

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

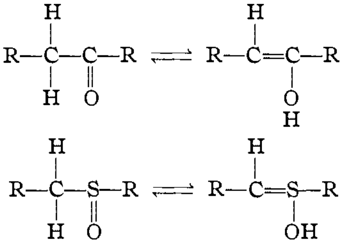
THE PREPARATION AND PROPERTIES OF CERTAIN SULFOXIDES AND SULFONES

BY R. L. SHRINER, H. C. STRUCK AND W. J. JORISON

RECEIVED JANUARY 20, 1930 PUBLISHED MAY 8, 1930

Although the enolization of a methylene group adjacent to a carbonyl group has been thoroughly studied, not much information is available on the behavior of compounds containing other linkages adjacent to a methylene group. The purpose of the present investigation was to study the influence exerted on a methylene group by the sulfoxide and sulfone linkages.

Using the customary notation, a comparison of the following formulas would indicate a similarity in chemical behavior; *i. e.*, under the proper conditions the sulfoxide might be expected to tautomerize in the same manner as the ketone



$$R{-}CH_2{-}C({=}O){-}R \rightleftharpoons R{-}CH{=}C(OH){-}R$$

$$R{-}CH_2{-}S({=}O){-}R \rightleftharpoons R{-}CH{=}S(OH){-}R$$

However, it has been known for some time that the chemical behavior of the sulfoxide linkage does not parallel that of the carbonyl.[1] Moreover, the electronic structures of sulfur–oxygen compounds, as formulated on the Lewis–Langmuir octet theory of valence, do not parallel exactly the electronic structure for carbon–oxygen.[2] The recent work of Sugden, who has found a considerable difference in the parachors of the carbonyl and the sulfoxide[3] groups, and the resolution by Phillips[4] of the sulfinic esters and sulfoxides, have furnished good evidence of the dis-

---

[1] For example, the Grignard reagent does not add to the sulfoxide linkage as it does to the carbonyl linkage. Courtot, "Le Magnesium en Chimie organique," Rigot and Co., **1926**, pp. 125, 225, ff.

[2] Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, **1923**, pp. 95, 100.

[3] Sugden, *J. Chem. Soc.*, **125**, 1177 (1924); **127**, 1525, 1868 (1925).

[4] Phillips, *ibid.*, **127**, 2552 (1925); **129**, 2079 (1926).