

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

**STEREISOMERISM OF DIPHENYL COMPOUNDS.
RESOLUTION OF 3,3'-DIAMINODIMESITYL. II¹**

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The diphenyl compounds which have thus far been resolved into pairs of mirror images have, in every case, been 2,6,2'-trisubstituted, or 2,6,2',6'-tetrasubstituted compounds, represented by the two general formulas I and II.



Of Type I only compounds in which A = carboxyl, B = nitro³ have been made; of Type II, several combinations have been prepared in which A = carboxyl, B = nitro;⁴ A = carboxyl, B = chlorine;⁵ A = carboxyl, B = methoxyl;⁶ A = amino, B = methyl;⁷ A = acetamino, B = methyl;⁷ A = acetamino, B = carboxyl;⁷ A = carboxyl, B = the —CH= group in a benzene nucleus;⁸ A = carboxyl, B = —CO— group in an anthraquinone nucleus.⁹ It is thus reasonably certain that there is no specific effect due to any particular group.

Owing chiefly to experimental difficulties, other diphenyl derivatives with three or four substitutions in the 2,6- and 2',6'-positions of the general tri- and tetrasubstituted type A,B,C, or A,B,C,D, have not been prepared and studied, but it can hardly be questioned that these could also exist in the form of optical isomers.

The only reasonably logical explanation of such isomerism is to assume that the two benzene rings are coaxial and not coplanar. The important problem then resolves itself into determining the mechanism by which various groups located in the 2,6- and 2',6'-positions as outlined above can prevent free rotation of the nuclei.

Turner and Le Fèvre¹⁰ suggested that the electrical nature of the sub-

¹ For previous papers see Hyde and Adams, *THIS JOURNAL*, 50, 2499 (1928).

² This communication is an abstract of a portion of a thesis submitted by Wendell W. Moyer in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

³ Christie and Kenner, *J. Chem. Soc.*, 123, 779 (1923); *ibid.*, 470 (1926); Christie, Holderness and Kenner, *ibid.*, 671 (1926).

⁴ Christie and Kenner, *ibid.*, 121, 614 (1922).

⁵ Christie, James and Kenner, *ibid.*, 123, 1948 (1923).

⁶ Kenner and Turner, *ibid.*, 2340 (1928).

⁷ Meisenheimer and Höring, *Ber.*, 60, 1425 (1927).

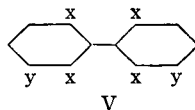
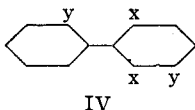
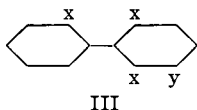
⁸ Kühn and Albrecht, *Ann.*, 464, 91 (1928).

⁹ Kühn and Albrecht, *ibid.*, 465, 282 (1928).

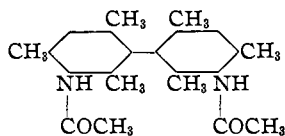
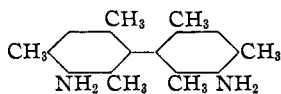
¹⁰ Turner and Le Fèvre, *J. Soc. Chem. Ind.*, 45, 831 (1926); *ibid.*, 45, 883 (1926).

stituted groups, the residual affinity on each ring and the internuclear forces were important influences. They believe the isomerism arises from an inherent property of the parent hydrocarbon. Such a theory would lead to the expectation of easy racemization in optically active diphenyl compounds. Bell and Kenyon¹¹ preferred to look on the isomerism as due, primarily, to the ortho-substituting groups acting as obstacles to free rotation, though they believed the size and electrical character of the substituting groups might have an influence. On the other hand, Mills¹² considered the isomerism to be entirely mechanical in character. He assumed that the 2,6- and 2',6'-groups are unable to get by each other due to their size and their proximity in space, and thus the two rings are never in the same plane.

In a previous paper¹ it was pointed out that on the basis of the mechanical theory three other types of diphenyl compounds should be capable of resolution, Formulas III, IV and V.



Here the substituting groups in the 2,6- and 2',6'-positions are the same and the individual rings are asymmetric, due to the substitution of some group in the proper position. In this investigation two compounds have been made which fall into the class represented by Formula V. The substances are 3,3'-diaminodimesityl (VI) and 3,3'-diacetaminodimesityl (VII).



The 3,3'-diaminodimesityl was readily resolved into its optical isomers. The *d*- and *l*-forms were both isolated pure; $d = [\alpha]_D + 42.3^\circ$, $l = [\alpha]_D - 41.5^\circ$, and from them the active diacetaminodimesityls were prepared. The *d*-diaminodimesityl was boiled for long periods with both alcoholic potassium hydroxide and hydrochloric acid. No racemization took place with the alkali and only an extremely slight change in the rotation was noted with the acid treatment.

The fact that groups in the 2,6- and 2',6'-positions in resolvable diphenyls may be the same, and that the compounds are not easily racemized, eliminates the possibility of explaining the isomerism as being caused entirely by the electrochemical character of the ortho substituted group. The presence of the two amino or acetamino groups produces

¹¹ Bell and Kenyon, *J. Soc. Chem. Ind.*, **45**, 864 (1926).

¹² Mills, *ibid.*, **45**, 884 (1926).

asymmetry in each of the rings, a condition which must be fulfilled if optical isomerism is to be possible, even though the rings are not in the same plane. These results offer strong additional evidence that the present mechanical theory may be correct.

To prepare diaminodimesityl, monobromomesitylene was converted to the Grignard, which by the action of cupric chloride gave, in better than 20% yields, dimesityl. This procedure is far more satisfactory than that described in the literature, the action of copper on mono-iodomesitylene. Considerable difficulty was encountered in the nitration of dimesityl, since all of the common nitrating reagents gave either a pure tetranitro derivative or a mixture of mono, di and tri. Acetyl nitrate proved satisfactory, however, and yielded a pure dinitro compound, even though an excess of reagent was used. Since by the use of this reagent mesitylene can be nitrated only to the mono nitro derivative, it seems certain that the dinitrodimesityl must be the 3,3'-substitution product. The reduction to the corresponding diamino was carried out in the usual way and the resolution of the latter was very readily accomplished through the dicamphorsulfonate. There was an extremely wide variation in the solubility of the diastereoisomeric salts and as a consequence the isolation of both forms in a pure state was a simple matter. The salts, on hydrolysis, gave the pure "d" and "l" bases. The active diacetamino derivatives were made by the action of acetic anhydride on the active diamino dimesityls.

It might be stated that attempts to condense nitro-iodomesitylene with copper to get the same dinitrodimesityl mentioned above were unsuccessful. Moreover, several experiments attempting the partial reduction of tetranitrodimesityl to 3,3'-dinitro-5,5'-diaminodimesityl resulted in mixtures. There was no difficulty in preparing 3,3'-dibromodimesityl but attempts to form the corresponding mono Grignard and from it the carboxylic acid gave negative results.

The facts that compounds of this type may be resolved and, moreover, that they may readily be prepared, make possible a much wider study of this general field. Other tetra-ortho-substituted compounds of a similar character are now being prepared. Compounds containing a di-ortho-substituted benzene nucleus attached to another residue, not a benzene, in which the atom combined to the benzene may have a fixed structure, are also being studied.

Experimental Part

Preparation of Dimesityl.—The application of the general method for preparing hydrocarbons discovered by Sakellarios and Kyrimis¹³ was found much more satisfactory for preparing dimesityl than the method described by Ullmann.¹⁴

¹³ Sakellarios and Kyrimis, *Ber.*, **57**, 322 (1924).

¹⁴ Ullmann, *Ann.*, **332**, 48 (1904).

In a 3-liter, three-necked flask fitted with a vigorous stirrer, reflux condenser and a 500-cc. dropping funnel were placed 48.7 g. of magnesium turnings and 125 g. of bromomesitylene in 150 g. of anhydrous ether, and a few crystals of iodine. By warming, without stirring, the reaction was started and allowed to proceed for a few minutes. Mechanical stirring was begun and a solution of 273 g. of bromomesitylene in 600 g. of dry ether was added at such a rate that the ether refluxed steadily. The addition of the halide required two and one-half to three hours, after which the solution was stirred for half an hour longer. The flask was then surrounded by ice and a suspension of 300 g. of finely powdered anhydrous cupric chloride in 600 cc. of dry ether was added as rapidly as the heating of the reaction mixture permitted. The flask was then warmed on a steam-cone until the ether refluxed gently and the stirring was continued for six hours. At the end of this time the mixture was cooled and poured slowly, with constant stirring, into cracked ice and strong hydrochloric acid. After the decomposition was complete, more hydrochloric acid was added in order to take all the cuprous chloride into solution. The ether layer was washed successively with hydrochloric acid, water, ammonia and water. After removing the ether, about 180 g. of low-boiling material distilled over and then 65 g. of dimesityl from 142–160° at 5 mm. The distillate solidified and upon crystallization from alcohol, 52 g. (22%) of dimesityl that melted at 99.5–100° was obtained.

Tetranitrodimesityl.—In small amounts at a time, 18 g. of dimesityl was added to 130 g. of fuming nitric acid (sp. gr. 1.50) which was stirred mechanically and cooled by a freezing mixture. When the dimesityl came in contact with the nitric acid, a dark coloration appeared for an instant and then quickly faded. Toward the end of the reaction some solid nitro compound separated from solution. The sides of the flask were washed down by 20 g. more of nitric acid and then, after standing for half an hour, the mixture was poured into cracked ice. The tetranitro compound separated as a slightly yellowish, flocculent precipitate which, after washing and drying, weighed 31.6 g. (quantitative yield). After recrystallization from glacial acetic acid, the compound was obtained pure and melted at 270–271°.

Anal. Subs., 0.2184: CO₂, 0.4146; H₂O, 0.0839. Calcd. for C₁₈H₁₈O₈N₄: C, 51.65; H, 4.34. Found: C, 51.77; H, 4.30.

Partial Reduction of Tetranitrodimesityl.—An attempt was made to reduce tetranitrodimesityl by means of alcoholic ammonium sulfide to 3,3'-diamino-5,5'-dinitrodimesityl in somewhat the same way that dinitromesitylene was reduced to nitro-amino-mesitylene.

In the first attempt, 8 g. of tetranitrodimesityl was added to a solution of 18 g. of ammonium hydroxide (sp. gr. 0.90) in 55 g. of absolute alcohol that had been saturated with hydrogen sulfide gas. The mixture was placed in an autoclave and heated at 140–150° for twelve hours. The brownish-red reaction mixture was acidified with dilute hydrochloric acid, the sulfur filtered off and the alcohol distilled from the acid solution. Upon adding ammonia, a reddish-yellow precipitate came down. This product was recrystallized from dilute alcohol and obviously was a mixture. An analysis showed that the tetranitro compound had been reduced on the average just beyond the triamino stage.

A second reduction using 10 g. of tetranitrodimesityl with 10 g. of ammonium hydroxide in 35 g. of absolute alcohol saturated with hydrogen sulfide, at 105–110° for twelve hours, also gave a mixture.

3,3'-Dibromodimesityl.—To a solution of 6.37 g. of dimesityl in 20 g. of carbon tetrachloride was added, with stirring and cooling in ice-water, a solution of 8.6 g. of bromine in 10 g. of carbon tetrachloride. The solution was allowed to stand in the dark overnight, after which the carbon tetrachloride was removed under reduced pressure.

A solution of 2 g. of sodium in 50 cc. of 95% alcohol was then added to the residue and the solution refluxed for half an hour. The mixture was poured into water and the product extracted with ether. The compound (6.6 g. or 63%) obtained was recrystallized from alcohol several times. When pure it melted at 112–113°.

Anal. Subs., 0.3160: CO₂, 0.6369; H₂O, 0.1443. Calcd. for C₁₃H₂₀Br₂: C, 54.55; H, 5.09. Found: C, 54.97; H, 5.11.

An attempt to make a mono Grignard in ether solution was not very successful. Only part of the magnesium went into solution. When all evidences of reaction were over, carbon dioxide was introduced just over the surface of the solution. Upon working up in the usual way a gummy product resulted from which no pure substance could be separated.

Tetra-aminodimesityl.—Six grams of the mixture of aminonitrodimesityls, obtained by the partial reduction of the tetranitrodimesityl, was reduced in a similar manner to that used in the preparation of diaminodimesityl. The tetra-amino compound thus obtained was slightly colored, and this color was removed by treating with 150 cc. of boiling alcohol, in which the amine was insoluble, and then adding a slight excess of concentrated hydrochloric acid which took all of the material into solution. Upon cooling the hydrochloride separated in glistening yellowish crystals. The hydrochloride was dissolved in water and the tetra-aminodimesityl precipitated by ammonia as a white, finely-divided material. Upon standing in the light, the compound became colored to a yellow-brown. The crude product (3.5 g.) was recrystallized from dilute pyridine and gave buff-yellow crystals that did not melt at 360°.

3,3'-Dinitrodimesityl.—Acetyl nitrate was found to nitrate mesitylene to give a quantitative yield of pure mononitromesitylene and consequently was used as a reagent for the preparation of 3,3'-dinitrodimesityl. Acetyl nitrate is much more easily prepared than benzoyl nitrate, a reagent which had been shown by Francis¹⁵ to react with mesitylene to give mononitromesitylene.

The acetyl nitrate was prepared according to the original method devised by Pictet and Khotinsky.¹⁶ It was used in acetic anhydride solution (approximately 1 g. of nitrogen pentoxide in 3–4 g. of acetic anhydride). The molar concentration per gram of the solution used was calculated so that it was easy to weigh out definite amounts of the acetyl nitrate. The acetyl nitrate solution was kept at –15°; at room temperature it turns brown and evolves red fumes.

A solution of 0.1 mole (23.8 g.) of dimesityl was made in 70 g. of carbon tetrachloride and cooled to 0° with a freezing mixture. Then with mechanical stirring and continued cooling, an amount of the acetyl nitrate solution that contained 0.3 mole of acetyl nitrate was slowly added. Care must be taken to add only a few cc. until the reaction starts. After a few minutes considerable heat was evolved and the mixture warmed to 35–40°. The remainder of the acetyl nitrate was then added at such a rate that the temperature remained at this upper limit. In trial runs it was demonstrated that it was necessary to have a temperature of 30–40° (as high as 50° without harm) toward the end of the nitration until completion in order to obtain the dinitro derivative pure— if nitration continued throughout at 0–10°, a low-melting product was obtained (m. p. 100–109°) that was probably the mononitro derivative or a mixture of dinitro- and mononitrodimesityl.

After the heat of the reaction had ceased, the stirring was continued at room temperature for another hour. The mixture was decomposed with water and the carbon tetrachloride steam-distilled out. The dinitrodimesityl was filtered off as a granular

¹⁵ Francis, *Ber.*, **39**, 3801 (1906).

¹⁶ Pictet and Khotinsky, *ibid.*, **40**, 1163 (1907); *Compt. rend.*, **144**, 210 (1907).

mass and weighed 32 g. (98%). Alternate recrystallizations from acetic acid and alcohol gave a pure product of constant melting point, 162.5–163.5° (corr.).

Anal. Subs., 0.2149: CO₂, 0.5193; H₂O, 0.1156. Calcd. for C₁₈H₂₀O₄N₂: C, 65.82; H, 6.14. Found: C, 65.90; H, 6.02.

Nitration of dimesityl in hot glacial acetic acid solution or in the cold with carbon tetrachloride as solvent and the theoretical amount of nitric acid gave mixtures of nitro products. Nitration with the theoretical amount (for the dinitro derivative) of potassium nitrate in concentrated sulfuric acid gave a mixture from which the tetranitro derivative was isolated.

3,3'-Diaminodimesityl.—To a solution of 180 g. of glacial acetic acid, 40 g. of water and 10 cc. of concentrated hydrochloric acid, was added 16.4 g. of pure dinitrodimesityl. Then with constant stirring, 100 g. of zinc dust was added in small amounts. The flask was at first cooled in an ice mixture and the zinc added so that the temperature went to 80–90°. This temperature was maintained by the heat of reaction as long as possible; then it was allowed to cool as the reaction ceased. More water was added from time to time. Zinc acetate separated after two hours and the reaction was stopped. The mixture was filtered and the residue washed with water and dilute hydrochloric acid. The filtrate was then made alkaline with an excess of ammonia in order to take all of the zinc salts into solution. The flaky white diaminodimesityl was filtered and again treated with acid and ammonia in order to remove any traces of zinc salts. The dried product weighed 13.2 g. Several recrystallizations from 60% alcohol raised the melting point to the constant value, 206–207° (corr.). The yield of pure diaminodimesityl was 8.2 g. (61%).

Anal. Subs., 0.1989: CO₂, 0.5880; H₂O, 0.1587. Calcd. for C₁₈H₂₄N₂: C, 80.53; H, 9.02. Found: C, 80.62; H, 8.93.

3,3'-Diacetylamino-dimesityl.—A mixture of 10 g. of acetic anhydride and 1 g. of pure diaminodimesityl was shaken for a few seconds. The diamino compound went into solution at once with evolution of heat, and then within two minutes the diacetyl derivative crystallized out from the anhydride solution. After standing for half an hour the compound was filtered and then washed thoroughly with water. The yield was quantitative and the derivative pure, as recrystallization from dilute methyl alcohol did not raise the melting point, 303–304°.

Anal. Subs., 0.1656: CO₂, 0.4563; H₂O, 0.1212. Calcd. for C₂₂H₂₈O₂N₂: C, 74.95; H, 8.01. Found: C, 75.15; H, 8.18.

Resolution of 3,3'-Diaminodimesityl.—To 200 cc. of boiling water containing 9.8 g. (0.042 mole) of *d*-camphorsulfonic acid was added 5.36 g. (0.02 mole) of diaminodimesityl. When complete solution was effected, Norite decolorizing charcoal was added and the solution filtered. The filtrate was allowed to stand in a cool place for thirty-six hours. At the end of this time a crop of large, light-yellow, transparent crystals had separated, which were essentially a pure salt, as shown by rotation and melting point as compared with recrystallized material. These crystals were filtered from the solution and washed with cold water; weight, 6.5 g. The salt did not have a sharp melting point, 175–187°, and gradually softened with gas evolution. The compound was found to be hydrated and, after drying, melted at 186–188° with previous softening.

Rotation. 0.2020 g. made up to 20 cc. with water at 20° gave $\alpha_D = +0.33^\circ$, $l = 2$; $[\alpha]_D^{20} = +16.3^\circ$.

The salt was recrystallized from 150 cc. of water. The melting point again was not sharp, but it melted exactly like the original material.

Rotation. (a) 0.2170 g. made up to 20 cc. with water at 20° gave $\alpha_D = +0.35^\circ$, $l = 2$; $[\alpha]_D^{20} = +16.1^\circ$. (b) 0.2265 g. made up to 20 cc. with 95% alcohol at 20° gave $\alpha_D = +0.73^\circ$, $l = 2$; $[\alpha]_D^{20} = +32.2^\circ$.

The salt was again crystallized from water. The melting point did not change.

Rotation. 0.2255 g. made up to 20 cc. with 95% alcohol at 20° gave $\alpha_D = +0.73^\circ$, $l = 2$; $[\alpha]_D^{20} = +32.4^\circ$.

Anal. (Parr Bomb). Subs., 0.5000: BaSO₄, 0.3056. Calcd. for C₃₃H₅₈O₃N₂S₂·H₂O: S, 8.54. Found: S, 8.40.

Anal. Subs., 0.2434 g. (air-dried salt): 140–150° for three hours lost 0.0054 g. Calcd. for C₃₃H₅₈O₃N₂S₂·H₂O: H₂O, 2.40. Found: H₂O, 2.22.

The mother liquor from the first crystallization, to which none of the subsequent recrystallization filtrates had been added, was then evaporated to 80 cc. and allowed to stand in the cold for a week. At the end of this time 0.4 g. of salt was removed and the liquid was further concentrated to 25 cc. Upon standing for another week a small amount of finely granular material separated. The weight was 0.2 g., m. p. 174–189° with no gas evolution. The rotation in alcohol was +25.9°. This was probably an impure sample of the more insoluble salt. The filtrate was shown to be a solution of the other diastereoisomeric salt in essentially pure form. No attempt was made to isolate the solid salt, but the solution was hydrolyzed directly to obtain the pure *l*-base.

***d*-3,3'-Diaminodimesityl.**—The pure crystalline (less soluble) dicamphorsulfonate salt was dissolved in an excess of hot water and the active diamino compound precipitated in white flakes with ammonia. After washing and drying, the compound was essentially pure, melting point 203.5–204.5 (corr.). Recrystallization from dilute alcohol did not raise the melting point and the product tended to acquire a slightly yellowish color.

Rotation. (a) 0.1907 g. made up to 20 cc. with 0.3 *N* hydrochloric acid at 20° gave $\alpha_D = +0.23^\circ$, $l = 2$; $[\alpha]_D^{20} = +12.0^\circ$. (b) 0.2456 g. made up to 20 cc. with acetone at 20° gave $\alpha_D = +1.04^\circ$, $l = 2$; $[\alpha]_D^{20} = +42.3^\circ$.

***d*-3,3'-Diacetaminodimesityl.**—The diacetyl derivative of the *d*-base was prepared in the same way as the racemic diacetate. The melting point of the compound, purified by crystallization from dilute alcohol, was 312–313° (corr.), with shrinking at 307°.

Rotation. 0.2370 g. made up to 20 cc. with absolute alcohol at 20° gave $\alpha_D = +0.73^\circ$, $l = 2$; $[\alpha]_D^{20} = +30.8^\circ$.

Anal. Subs., 0.1727: CO₂, 0.4738; H₂O, 0.1254. Calcd. for C₂₂H₂₈O₂N₂: C, 74.95; H, 8.01. Found: C, 74.82; H, 8.12.

***l*-3,3'-Diaminodimesityl.**—The final mother liquors from the resolution were diluted to 100 cc. and the diamino precipitated with ammonia. After recrystallization from dilute methyl alcohol, it melted at 203–204° (corr.).

Rotation. 0.2265 g. made up to 20 cc. with acetone at 20° gave $\alpha_D = -0.94^\circ$, $l = 2$; $[\alpha]_D^{20} = -41.5^\circ$.

***l*-3,3'-Diacetaminodimesityl.**—This derivative was made by the same method as described for the *d*-form. It melted at 311–313° (corr.), with previous shrinking at 307°.

Rotation. 0.2300 g. made up to 20 cc. with absolute alcohol gave $\alpha_D = -0.70^\circ$, $l = 2$; $[\alpha]_D^{20} = -30.4^\circ$.

Racemization Experiments.—The optical stability of the *d*-3,3'-diaminodimesityl was studied under two different sets of conditions.

1. A solution of 0.3 g. of the *d*-base in a mixture of 20 cc. of absolute alcohol and 3 g. of potassium hydroxide in 3 cc. of water was refluxed for five hours. The rotation of the recovered diamine showed that practically no racemization had occurred.

Rotation. 0.2262 g. made up to 20 cc. with acetone at 20° gave $\alpha_D = +0.92^\circ$, $l = 2$; $[\alpha]_D^{20} = +40.7^\circ$.

2. A solution of 0.2 g. of *d*-diaminodimesityl in 30 cc. of concentrated hydrochloric acid was refluxed for nine hours. Racemization took place to a very slight extent.

Rotation. 0.1645 g. made up to 20 cc. with acetone at 20° gave $\alpha_D = +0.64$, $l = 2$; $[\alpha]_D^{20} = +38.9^\circ$.

Nitro-aminomesitylene.—Dinitromesitylene was prepared by the action of cold fuming nitric acid on mesitylene at 0°, according to the method by Fittig.¹⁷

The partial reduction of dinitromesitylene to nitro-aminomesitylene was most readily accomplished by a modification of the original procedure of Küster and Stallberg.¹⁸ A solution of 100 g. of aqueous ammonia (sp. gr. 0.90) in 300 g. of absolute alcohol was cooled in an ice-bath and saturated with hydrogen sulfide. The ammonium sulfide solution was then placed in an autoclave with 80 g. of dinitromesitylene and the mixture heated at a temperature of 110–115° for fifteen hours. The yield (89%) was better than that reported previously.

Nitro-iodomesitylene.—To a hot solution of 150 cc. of water, 70 cc. of concentrated hydrochloric acid, and 5 cc. of alcohol, was added 27 g. (0.15 mole) of nitro-aminomesitylene and the solution cooled to 0°. As the solution cooled, the hydrochloride separated. To the cold mixture was then added with constant stirring, 10.5 g. of sodium nitrite in 20 cc. of water. The diazonium salt solution was filtered from insoluble material. Then with stirring a solution of 30 g. of potassium iodide in 50 cc. of water was added. A red solid separated and then as the mixture approached room temperature, nitrogen was evolved and the color changed to yellow. The mixture was warmed to 45° and allowed to stand for several hours. The product was filtered and treated with hot sodium hydroxide solution

¹⁷ Fittig, *Ann.*, **141**, 133 (1867).

¹⁸ Küster and Stallberg, *ibid.*, **278**, 213 (1894).

and acid successively. After recrystallization from alcohol a yield of 32.5 g. (72%) of buff-colored crystals was obtained, melting at 96–97°.

Anal. Subs., 0.2230: CO₂, 0.3133; H₂O, 0.0715. Calcd. for C₉H₁₀O₂NI: C, 37.11; H, 3.46. Found: C, 38.31; H, 3.59.

Several attempts to make 3,3'-dinitrodimesityl by the action of Naturkupper C on nitro-iodomesitylene between temperatures of 200–300° gave only tars from which no definite compound was obtained. An attempt with nitrobenzene as a solvent yielded no better results.

Summary

1. 3,3'-Diaminodimesityl has been prepared and resolved through the dicamphorsulfonate to yield pure *l*- and *d*-modifications.

2. The active diamines were converted into the corresponding active diacetamino derivatives.

3. These are the first diphenyl derivatives resolved with the 2,6,2',6'-positions, all occupied by the same group. This lends support to the mechanical theory for explaining the optical isomerism in certain diphenyl compounds.

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NOTE

The Electrolysis of Metallo-Organic Compounds.¹—Gaddum and French² have recently reported a series of experiments on the electrolysis of ether solutions of the Grignard reagent. In their paper they comment on the chemical reactivity of the metallic magnesium which was deposited at the cathode but do not describe its physical properties. Some time ago the authors made a series of experiments on the electrolysis of magnesium ethyl bromide in ether solutions, using platinum electrodes. The solutions showed a good conductivity and a beautiful crystalline deposit of metallic magnesium quickly formed upon the platinum cathode. This deposit adhered quite firmly to the electrode surface. Products were detected in the solution similar to those reported by Gaddum and French, which are to be attributed to the anode reaction, but it is impossible to say whether these were produced by direct electrolysis or by a secondary reaction of bromine, which had been liberated at the anode, with the Grignard reagent. In order to get away from the effects of the halogen liberated at the anode, zinc diethyl was used in place of the Grignard reagents in some of the electrolysis experiments. Zinc diethyl in the pure state shows no appreciable conductivity but an ether solution showed a specific conductivity of 10⁻⁴. With an applied potential of 110 volts

¹ The experimental results noted here were originally included in a paper which was submitted to THIS JOURNAL for publication in June, 1926.

² Gaddum and French, THIS JOURNAL, 49, 1295 (1927).