

ner. Without attempting to distil the dried ether extract it was added to an ether solution of *p*-toluidine. Benzylsulfonfyl *p*-toluidide, m. p. 113–114°, was obtained by alkaline extraction and after removing the excess of *p*-toluidine and evaporation of the ether solution an oily residue remained which gave a strong test for halogen and smelled strongly of benzyl chloride. After standing for two days *p*-tolylurethan, m. p. 50–52°, crystallized from the oil and was identified by a mixed melting point with the known substance.

Chlorination of Acyldithiourethans.—Ethyl benzoyldithiocarbamate was chlorinated and the resulting oil, dissolved in ether, was added cautiously to an ether solution containing three equivalents of *p*-toluidine and the solution allowed to stand over sodium bicarbonate solution for twenty-four hours. Ethylsulfonfyl *p*-toluidide was obtained from the mixture by extraction with sodium hydroxide. On adding 6 *N* hydrochloric acid to the remaining ether solution a white solid separated, particularly on diluting the acid. This solid was practically insoluble in water or dilute acid and crystallized from alcohol as glass-like prisms, softening slightly at 190° and melting at 193–194°. Analysis for chlorine and nitrogen gave results

indicating that this compound was the monohydrochloride of benzoyl di-*p*-tolylguanidine.

In Table I are registered the representatives of the different types of sulfur compounds exposed to the action of chlorine gas, and the different products formed by such drastic treatment. In Table II are recorded several new compounds that were obtained during the progress of our research.

Summary

1. A study of the action of chlorine in aqueous solution on different organic sulfur compounds has been continued.

2. In this paper is described the behavior of chlorine gas toward sulfur compounds of the thiol type or their derivatives, and derivatives of the xanthate series, thiosulfonates and acyl dithiourethans.

3. Further research is in progress and will be reported later.

NEW HAVEN, CONN.

RECEIVED APRIL 16, 1938

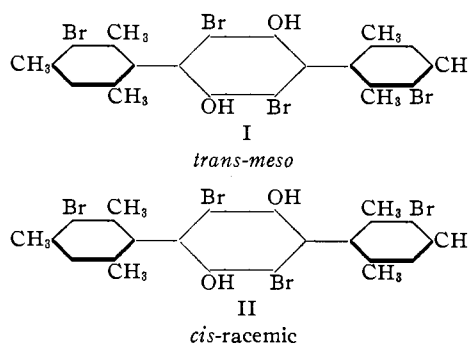
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Stereochemistry of Biphenyls.¹ XLIV. *Meso* and *Racemic* Isophthalamides of 3-Nitro-3'-aminobimesityl

BY ROGER ADAMS AND R. M. JOYCE, JR.*

Several molecules previously have been described in which two points of restricted rotation occur.² These were found to exist in two diastereoisomeric forms as anticipated and since the molecules were symmetrical one was *meso* and other *racemic*. In all these cases, however, the two points of restriction were on a single benzene nucleus as illustrated by the two 3,6-di-(3-bromo-2,4,6-trimethylphenyl)-2,5-dibromohydroquinones I and II. These substances were widely different in solubility. Compound II was resolved, while compound I resisted resolution.

A study now has been made to determine the characteristics of molecules with two points of restricted rotation not as closely adjacent as in diphenyl benzenes. Such a molecule was conveniently prepared by condensation of isophthalyl chloride and 3-nitro-3'-aminobimesityl. Two di-



astereoisomers were isolated which may be assigned the formulas III and IV. It is thus evident that separation of the points of restricted rotation in a molecule does not alter the number of stereoisomers to be expected.

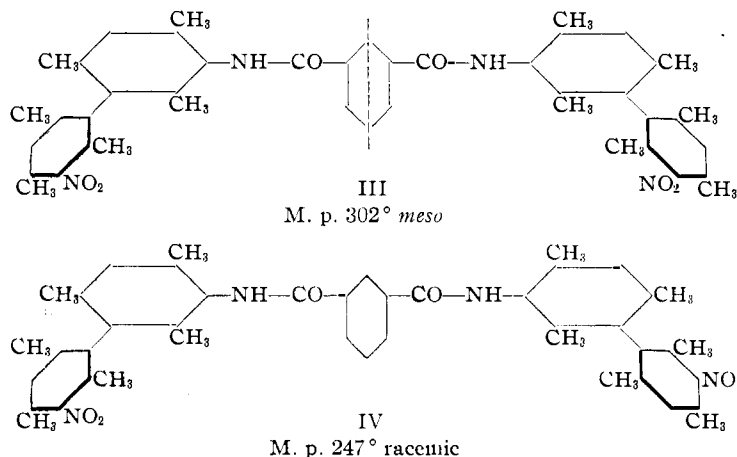
These isomers showed a marked difference in solubility; the higher-melting was six times as soluble in toluene as the lower-melting. A mixed melting point of 90% of the lower and 10% of the higher showed a depression.

The compound III may be divided into two identical halves (dotted line in III) and is therefore *meso*. The compound IV has no elements

* Submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry. Chemical Foundation Fellow, 1936–1938.

(1) For previous paper in this series see Adams and Snyder, *THIS JOURNAL*, **60**, 1411 (1938).

(2) Browning and Adams, *THIS JOURNAL*, **52**, 4098 (1930); Schildneck and Adams, *ibid.*, **53**, 343, 2203 (1931); Knauf, Schildneck and Adams, *ibid.*, **56**, 2109 (1934); Chang and Adams, *ibid.*, **56**, 2089 (1934).



of symmetry and is therefore racemic. The formulas for the *meso* and racemic forms have been assigned arbitrarily as no experimental evidence is available to distinguish the two.

The condensation of 3-nitro-3'-aminobimesityl with adipyl chloride resulted in the isolation of only a single product; with oxalyl chloride, on the other hand, two products were formed but they were difficult to separate from each other and did not have sharp melting points.

Experimental

3,3'-Dinitrobimesityl.—The following modification of the procedure described by Moyer and Adams³ was devised. To a solution of 11.9 g. of bimesityl in 40 cc. of carbon tetrachloride in a 200-cc., round-bottomed flask, equipped with dropping funnel, stirrer and thermometer, was added at such a rate that the temperature was maintained at 35–40°, a nitrating mixture prepared by adding 6.3 cc. of 100% nitric acid to 25 cc. of cold acetic anhydride (kept below 12°). After the addition was complete the temperature was maintained at 35–40° for one hour and the solution then poured into ice water and shaken to decompose the acetic anhydride. The carbon tetrachloride was removed by steam distillation and the dinitro compound solidified. It was purified by recrystallization from ethanol; occasionally, when the crude material was less pure, from acetic acid and then from ethanol: yield, 11–13 g. (67–79% theory); m. p. 162–163° (corr.).

3-Nitro-3'-aminobimesityl.—In a 200-cc., round-bottomed flask, equipped with a two-holed stopper holding an inlet tube extending to the bottom of the flask and a gas exit tube, was placed 75 g. of glacial acetic acid and 11.4 g. of anhydrous stannous chloride. Dry hydrogen chloride was passed in until the salt dissolved.

The solution thus obtained was then dropped during one hour into a solution of 6.6 g. of 3,3'-dinitrobimesityl in 60 cc. of warm glacial acetic acid in a flask provided with a dropping funnel, stirrer and reflux condenser protected with a calcium chloride tube and immersed in a bath maintained at 50°. Stirring was continued for three

hours longer with the reaction mixture at the same temperature. The tin complex starts to separate when about half the reducing agent has been added. Upon cooling, the tin complex separated completely and was filtered and washed with a little acetic acid and then with water. The filtrate upon dilution with water yielded 2 g. of unchanged dinitrobimesityl.

The tin complex was washed with water and then decomposed by boiling for five minutes with a solution of 100 cc. of ethanol and 25 cc. of 2 *N* aqueous sodium hydroxide; Norite was added to facilitate the coagulation of the precipitated stannic oxide and the solution filtered hot. The alcohol solution was concentrated to 25 cc. and 15 cc. of water added. Upon cooling,

bright yellow crystals separated which were purified by crystallization from 50% ethanol, m. p. 145–146°. From the filtrates a second crop of nitroamine was obtained, bringing the total yield to 3 g. (72% based on unrecovered nitro compound).

Anal. Calcd. for C₁₈H₂₂N₂O₂: C, 72.48; H, 7.39; N, 9.40. Found: C, 72.70; H, 7.58; N, 9.50.

The hydrochloride was prepared by dissolving the amine in a small volume of hot ethanol and adding a slight excess of dilute hydrochloric acid, then an equal volume of water. The salt crystallized on cooling. It softens at 236° and melts at 244–247° (with dec.).

Anal. Calcd. for C₁₈H₂₃N₂O₂Cl: Cl, 10.60. Found: Cl, 10.40.

Isophthalamides of 3-Nitro-3'-aminobimesityl.—To a solution of 6.27 g. (0.02 mole) of 3-nitro-3'-aminobimesityl in 10 cc. of dry benzene containing 0.2 g. (0.025 mole) of dry pyridine was added 2.05 g. (0.01 mole) of isophthalyl chloride in 5 cc. of dry benzene and the mixture stirred for a few minutes, then poured into water. The benzene was removed by steam distillation and the product collected on a filter and dried. The crude material was boiled with 250 cc. of toluene and a small quantity of insoluble product was filtered. The filtrate was concentrated to 100 cc. and cooled, whereupon 0.645 g. of a fine gray-white powder separated. By further concentration to 50 cc. an additional 0.293 g. was obtained. The toluene solution was then diluted to a volume of 175 cc. with more toluene, heated to boiling, and ligroin (b. p. 60–100°) added in an amount just insufficient to produce a permanent turbidity. As the solution cooled, small white crystals separated which weighed 0.793 g.

The filtrate from this crop was concentrated to about 100 cc. and again treated with ligroin. This fourth fraction weighed 1.32 g. By a similar procedure, concentrating to 50 cc., a fifth fraction was obtained, weighing 2.47 g.

The first three fractions were combined and recrystallized several times from toluene until a constant melting point of 247° (corr.) resulted. The product formed a very fine white powder.

Anal. Calcd. for C₄₄H₄₆N₄O₈: C, 72.73; H, 6.33; N, 7.71. Found: C, 72.58; H, 6.22; N, 7.96.

The fourth and fifth fractions, which contained the major portion of the product, were combined and recrystal-

(3) Moyer and Adams, *THIS JOURNAL*, **51**, 630 (1929).

lized several times from a toluene-ligroin (3:1) mixture. About 1 g. of fine white crystals, m. p. 302°, was obtained.

Anal. Calcd. for $C_{24}H_{16}N_4O_6$: C, 72.73; H, 6.33; N, 7.71. Found: C, 72.86; H, 6.11; N, 7.95.

A melting point of a mixture of 90% of the lower- and 10% of the higher-melting product showed a depression, m. p. 228–238°.

The higher-melting compound was approximately six times as soluble in toluene as the lower-melting.

Condensation of Adipyl Chloride with 3-Nitro-3'-aminobimesityl.—The procedure used was similar to that described for the isophthalyl derivative. The crude product was crystallized several times from acetone and a single compound was obtained, m. p. 230–231° (corr.). Attempts to isolate a second isomer from the filtrates were unsuccessful. The fractions thus obtained melted over a two or three degree range in the neighborhood of 226°, but mixed melting point with the 230–231° product showed no depression.

Anal. Calcd. for $C_{42}H_{30}N_4O_6$: C, 71.39; H, 7.08. Found: C, 71.70; H, 7.32.

Condensation of Oxalyl Chloride with 3-Nitro-3'-aminobimesityl.—By a procedure similar to those just described one mole of oxalyl chloride was condensed with two of amine. The crude product was obtained in almost quantitative yields. It was fractionally crystallized from dibutyl ether and two fractions obtained, one m. p. 304–307° (corr.), and the other m. p. 273–283° (corr.). The melting point of the lower-melting form could not be improved over the value given, so that it may not have been entirely pure in spite of a satisfactory analysis.

Anal. (High-melting fraction) Calcd. for $C_{38}H_{22}N_4O_6$: N, 8.62. Found: N, 8.83. (Low-melting fraction) Found: N, 8.73.

3-Nitro-3'-isothiocyanobimesityl.—An attempt was made to prepare the thiourea from carbon disulfide and 3-nitro-3'-aminobimesityl. Only an isothiocyano derivative was obtained.

To a solution of 1.5 g. of 3-nitro-3'-aminobimesityl in 10 cc. of ethanol was added 10 cc. of carbon disulfide and 5.5 cc. of alcoholic potassium hydroxide (0.22 *N*). The solution was refluxed for eight hours, evaporated to a small volume and cooled. The product separated and was recrystallized from ethanol to a constant m. p. of 119–120°.

Anal. Calcd. for $C_{19}H_{20}N_2O_2S$: C, 67.05; H, 5.88; S, 9.41; mol. wt., 340. Found: C, 67.49; H, 6.52; S, 9.08; mol. wt. (Rast), 345.

Summary

Two diastereoisomers have been obtained by the condensation of one mole of isophthalyl chloride and two moles of 3-nitro-3'-aminobimesityl. These represent *meso* and racemic isomers due to the presence of two points of restricted rotation in the molecules. They differ from analogous isomers previously prepared in that the points of restricted rotation are widely separated from each other.

URBANA, ILLINOIS

RECEIVED APRIL 14, 1938

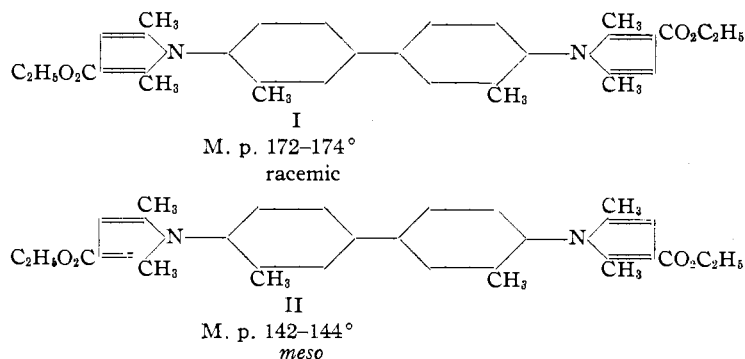
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Stereochemistry of Biphenyls.¹ XLV. Stereoisomeric Dipyrrolyl Biphenyls

BY ROGER ADAMS AND R. M. JOYCE, JR.*

The study of molecules containing two points of restricted rotation² has been extended to certain dipyrrolyl biphenyls. Both *o*-tolidine and dianisidine were condensed with 3-carbethoxy-2,5-hexanedione and in each case two diastereoisomeric forms were isolated. By way of illustration the isomers from *o*-tolidine are shown in I and II. These pairs of isomers represent molecules in which free rotation between the benzene nuclei exists and consequently such molecules are much more mobile than the diphenyl-

pyrroles previously prepared in diastereoisomeric forms.



* Submitted in partial fulfillment of the requirements for the Ph.D. degree in Chemistry. Chemical Foundation Fellow, 1936–1938.

(1) For previous paper in this series see Adams and Joyce, THIS JOURNAL, **60**, 1489 (1938).

(2) Chang and Adams, *ibid.*, **56**, 2084 (1934); Browning and Adams, *ibid.*, **52**, 4098 (1930); Shildneck and Adams, *ibid.*, **53**, 343, 2203 (1931); Knauf, Shildneck and Adams, *ibid.*, **56**, 2109 (1934).

The two isomers differ from each other in melting point and solubility. The higher-melting form arbitrarily has been assigned the racemic structure. It is less soluble than the lower-melting form. The difficulty of obtaining easily