lation of the final products. In larger runs it may be more convenient to hydrogenate the aqueous solution of sodium salts using a nickel catalyst and several hundred pounds hydrogen pressure.

The ether and any residual water were removed by evaporation at reduced pressure to yield 90 g. of crude acids. These were dissolved in 100 cc. of hot toluene, and the hot solution was treated with carbon black and filtered. On cooling to room temperature, the sebacic acid separated as a beautiful white crystalline product, m.p. 131.5–132.5°; 30 g. (30% based on butadiene). The remaining acids comprise a complex mixture from which the individual isomers cannot be separated in good yields by any simple procedure. Thus, some of the sebacic remains associated with the ethylsuberic and cannot be directly crystallized despite the large difference in solubility. Another difficulty arises from the fact that most of the diethyladipic is present as the very soluble, racemic isomer. The following procedure comprises the most suitable laboratory separation:

An additional 50 cc. of toluene was added to the filtrate from the sebacic acid crystallization. This solution was then agitated for 2 hr. with a mixture of 10 cc. of water and 50 g. of urea at 30°. The mixture was filtered and the solid washed with small volumes of toluene. The solid urea–sebacic acid adduct was decomposed by warming with 100 cc. of water and filtering the urea solution from the liberated sebacic acid; 7 g. of additional sebacic acid was recovered in this manner.

The original filtrate from the adduction comprises a toluene phase containing diethyladipic acid and a heavy oily phase which is the salt of urea and ethylsuberic acid. This salt phase was separated from the toluene solution and decomposed by carefully adding 100 cc. of 80% sulfuric acid. The crude ethylsuberic acid was removed by filtration and dried (weight = 42 g.); it was recrystallized from 150 cc. of toluene at 5° to yield 35 g. of acid, m.p. 75–77°.

It is difficult to recover racemic diethyladipic acid from toluene solution since other acids present at this stage interfere with its crystallization. Small yields may be obtained by crystallization at 0° from a mixture of toluene and hexane and then recrystallized from anhydrous acetonitrile at 0° to give the pure compound. However, a more effective acid separation is obtained by first converting the racemic to the *dl-meso*-mixture and crystallizing the *meso* acid. In the present example, racemization of the diethyladipic acid was affected by distilling the toluene from the acids, then heating the acids under nitrogen at 250° for 1.5 hr. Pure *meso*-diethyladipic acid (5 g.) was obtained by crystallization from 30 cc. of toluene; m.p. 138–139°.

The filtrate at this point is largely racemic diethyladipic acid with small amounts of ethylsuberic and sebacic acids, and of monobasic acids resulting from transmetalation side reactions. Such residues from a number of runs were combined and the racemic diethyladipic isolated by recrystallization from acetonitrile; m.p., 72–73°. This acid was resolved by recrystallization of the brucine salts; $[\alpha]^{25}_{D} = \pm 19°$; m.p., 76–77°. Racemic diethyladipic is quite soluble in water and in most organic solvents in contrast to the *meso* acid which resembles sebacic in its general solubility behavior.

After removal of acetonitrile from the filtrate the small remaining residue was distilled at reduced pressure. Small amounts of pelargonic acid (b.p. 130°/8 mm.) and α-ethylheptanoic acid (b.p. 123°/8 mm.) amounting to approximately 1% and 0.5% of the total product were isolated[34] and identified as the piperazonium salts (m.p., 95–96° and 69–70°, respectively).

CINCINNATI 37, OHIO

---

(34) F. M. Trent, F. D. Miller, and G. H. Brown, *Chem. Eng. Data*, 5, 110 (1960).

[CONTRIBUTION FROM THE RESEARCH DIVISION, U.S. INDUSTRIAL CHEMICALS CO.]

A New Synthesis of Dibasic Acids. II.
2,5-Diphenyladipic Acid and Related Compounds[1]

CHARLES E. FRANK, JACK R. LEEBRICK,[2] LOUIS F. MOORMEIER, JOHN A. SCHEBEN, AND OTTO HOMBERG

Received February 25, 1960

2,5-Diphenyladipic acid and 2,5-dimethyl-2,5-diphenyladipic acid have been synthesized by the metalative dimerization of styrene and α-methylstyrene, respectively, with sodium and subsequent reaction with carbon dioxide.

The first paper in this series[3] reports the discovery of a new synthesis of dibasic acids involving the metalative dimerization of conjugated dienes to obtain the dimetallo dimer followed by carbonation. The present paper is concerned with the extension of this reaction to styrene and substituted styrenes to yield dibasic acids containing aromatic substituents on the carbon chain. The more important of these products are 2,5-diphenyladipic acid and 2,5-dimethyl-2,5-diphenyladipic acid obtained by the metalative dimerization of styrene and of α-methylstyrene, respectively. 2,5-Diphenyladipic acid has been reported only once previously and was obtained *via* the malonic ester synthesis through 2,5-dicarboxy-2,5-diphenyladipic acid.[4] 2,5-Dimethyl-2,5-diphenyladipic acid is a new product, of special interest because of the absence of any *alpha* hydrogen atoms. Both diphenyladipic and dimethyldiphenyladipic acids are readily converted

---

(1) The work was initiated under a Fellowship supported by the U.S. Industrial Chemicals Company at the Applied Science Research Laboratory of the University of Cincinnati. Development of the reaction and synthesis of the various derivatives were conducted at the Research Division of the sponsoring company.

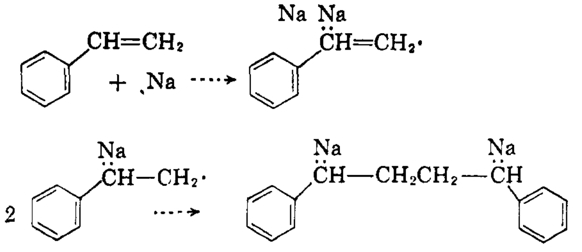
(2) Present address: Metal & Thermit Corporation, Rahway. N. J.

(3) C. E. Frank and W. E. Foster, *J. Org. Chem.*, 26, 303 (1961).

(4) S. M. McElvain and P. M. Laughton, *J. Am. Chem. Soc.*, 73, 448 (1951).

to the corresponding dicyclohexyl derivatives by hydrogenation.

It is of interest to note that the addition of sodium (more accurately, an electron) to the double bond occurs almost exclusively at the *alpha* carbon, as would be predicted on the basis of the bond polarization:



This is one of the structures postulated by Szwarc in his study of "living polymers" from styrene.[5]

Diphenyladipic acid possesses an unusual combination of aliphatic and aromatic properties which makes it of considerable interest both in the plastics field and as a synthetic intermediate. The first area includes not only polyesters and polyamides, but also simple esters which are of particular promise for vinyl plastisols and organosols. In addition to ester formation, reactions of diphenyladipic acid described in the present paper include chlorination to the hexachloro derivative and decarboxylation to 2,5-diphenylcyclopentanone. 2,5-Dicyclohexyladipic acid also decarboxylates to give 2,5-dicyclohexylcyclopentanone in excellent yields; both high and low melting forms of this new ketone were isolated.

Diphenyladipic acid was separated for the first time into racemic and *meso* forms employing fractional crystallization from benzene-ethanol mixtures. The low melting form, presumably the racemic mixture, melts at 208°, the high melting form at 266–267°.

EXPERIMENTAL

Disubstituted dibasic acids. 2,5-Diphenyladipic acid.[6] In a typical example, 0.5 mole (52 g.) of styrene was diluted with 300 cc. of ethylene glycol diethyl ether and added over a 4-hr. period to a well stirred dispersion of 23 g. of sodium (dispersed[7] in 100 cc. dibutyl ether) in 700 cc. of ethylene glycol diethyl ether containing 4 g. of *o*-terphenyl; the temperature was held at −40 to −50°. The reaction mixture was carbonated on a large excess of Dry Ice, and the excess carbon dioxide allowed to evaporate over night prior to quenching by the addition of 400 cc. of water. (Caution!) The aqueous and solvent layers were separated, and the aqueous layer filtered and acidified with concentrated hydrochloric acid to precipitate the crude diphenyladipic acid.

The crude product was first washed with 200 cc. of hot (80°) toluene to remove polymeric acids, then with water to remove salt. Completeness of the water wash is most conveniently checked by testing the filtrate for chloride ion. The washed acid at this stage had a neutral equivalent of 155; weight, 30 g. (40%). This product was recrystallized from 300 cc. of a 6:1 benzene-alcohol mixture to yield 26 g. of the racemic-*meso* mixture melting at 202–224°.

The once recrystallized, racemic-*meso* product may be separated into the two forms by repeated fractional crystallization from benzene-ethanol mixtures and final recrystallization from acetic acid.

Racemic form. m.p. 208°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.29: H, 5.99.

Meso form. m.p. 266–267°.

Anal. Found: C, 72.53, H. 6.22.

As a further evidence of the specificity of the reaction, a sample of disodiodiphenylbutane was treated with water and the resultant diphenylbutanes separated and purified. Over 90% of the dimeric product was obtained boiling at 140°/15 mm. and melting (recrystallization from ethanol) at 52–53°; this product gave no melting point depression with an authentic sample of 1,4-diphenylbutane.

As in the synthesis of sebacic and isomeric acids from butadiene,[3] the major side-reaction is polymerization; reaction conditions here are even more critical in view of the greater tendency of styrene to polymerize.[8] Suppression of polymerization is effected by rigid exclusion of moisture and other reactive contaminants, by high dilution of the styrene, and by the use of an excess of finely dispersed sodium.[6] Best yields employing normal (10–20 micron) sodium dispersion have fallen in the range of 35–50%. Maximum yields (80–85%) of diphenyladipic acid have been obtained operating in dimethyl ether as the reaction medium and employing 1–3 micron sodium dispersion.[6b] In view of the pyrophoric nature of organosodium compounds and of the extreme flammability of dimethyl ether, this method should be employed only in all metal equipment, and the reaction mixture should never be allowed to come in contact with air.

2,5-Dicyclohexyladipic acid.[9] A 50-g. sample of *dl*-2,5-diphenyladipic acid, 5 g. of 5% palladium-on-carbon catalyst (Englehard Industries) and 150 cc. of glacial acetic acid were charged into a pressure hydrogenator (glass liner) and the mixture heated with agitation at 120° and 1000–1500 p.s.i. hydrogen pressure until hydrogenation was complete. The resultant solution was filtered to remove catalyst, and water was added to the filtrate to precipitate the product. Recrystallization from an equal volume of acetone and petroleum ether (b.p. 35–52°) yielded the *dl* acid as beautiful white needles, m.p. 134–135°C.

Anal. Calcd. for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74. Found: C, 69.60; H, 9.90.

In a similar experiment, hydrogenation of 50 g. of the *meso*-diphenyladipic acid in 100 cc. of acetic acid using palladium catalyst yielded the *meso*-dicyclohexyladipic acid. Recrystallization from acetone gave the pure *meso*-dicyclohexyladipic acid, m.p. 165–166°.

Anal. Calcd. for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74. Found: 69.75; H, 9.85.

2,5-Dimethyl-2,5-diphenyladipic acid. As in the first example, 0.5 mole (59 g.) of α-methylstyrene diluted with 300 cc. of ethylene glycol diethyl ether was added over a 4-hr. period to an excess of well stirred dispersion of 23 g. of sodium (dispersed in dibutyl ether) in 700 cc. of ethylene glycol diethyl ether containing 4 g. of *o*-terphenyl as the "carrier." The reaction mixture was carbonated by pouring onto a large excess of Dry Ice and the excess carbon dioxide allowed to evaporate over night prior to quenching by the addition of 200 cc. of water. The aqueous and organic layers were separated, and the aqueous layer filtered and acidified

---

[5] M. Szwarc, M. Levy, and R. Milkavich, *J. Am. Chem. Soc.*, **78**, 2656 (1956).

[6] C. E. Frank and J. R. Leebrick, (a) U. S. Patent **2,816,913** (Dec. 17, 1957); (b) U. S. Patent **2,816,914** (Dec. 17, 1957).

[7] O. D. Frampton and J. F. Nobis, *Ind. Eng. Chem.*, **45**, 404 (1953).

[8] W. A. Schulze and W. W. Crouch, *J. Am. Chem. Soc.*, **70**, 3891 (1948).

[9] J. F. Nobis and R. W. Horst, U. S. Patent **2,810,749** (Oct. 12, 1957).

to precipitate crude dimethyldiphenyladipic acid. The crude product was washed with 200 cc. of hot benzene to remove polymeric acids, and with a large volume of hot water to remove inorganic salts.

After vacuum drying, the washed 2,5-dimethyl-2,5-diphenyladipic acid had a neutral equivalent of 164.5 (theory 163); m.p. 190–214°; yield, 41 g. (50%). This product was largely the low melting (presumably *dl*) isomer. Recrystallization from 550 cc. of acetonitrile yielded 35 g. of the pure acid, m.p. 216–217°.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.59; H, 6.79. Found: C, 73.52; H, 7.04.

Accumulation and reworking of several filtrates gave a very small fraction (2–5%) of the product as the *meso* isomer, m.p. 247–449° from methanol.

Anal. Found: C, 73.27; H, 6.97.

The almost complete absence of the *meso* form indicates an interesting stereospecificity of the dimerization step. In the case of diphenyladipic from styrene and of divinyladipic from butadiene, the *dl* product also predominates.

A portion of the disodiodiphenylhexane also was hydrolyzed to give an 88% yield of 2,5-diphenylhexane, b.p. 148–151°/5 mm.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 90.81; H, 9.34.

2,5-Dimethyl-2,5-dicyclohexyladipic acid. Hydrogenation of racemic dimethyldiphenyladipic acid was carried out in acetic acid solution using palladium-on-carbon catalyst as in the preparation of dicyclohexyladipic acid. The product was recrystallized from methanol to yield pure racemic 2,5-dimethyl-2,5-dicyclohexyladipic acid, m.p. 223–224°.

Anal. Calcd. for $C_{20}H_{32}O_4$: C, 70.96; H, 10.12. Found: C, 70.82; H, 9.89.

Derivatives of diphenyladipic acid. Di-n-butyl-2,5-diphenyladipate. One equivalent (149.6 g.) of 2,5-diphenyladipic acid (m.p. 206–235°), 92.7 g. (1.25 moles) of *n*-butyl alcohol, 0.7 g. of *p*-toluenesulfonic acid and 1.0 g. of Nuchar-CA were refluxed under nitrogen, water produced being collected in a Dean-Starke trap. The reaction was essentially complete in 3.7 hr., final reflux temperature being 142°. The mixture was stirred with 2.0 g. of sodium carbonate and 10 g. of Cellite for 15 min. and filtered. Excess alcohol was removed under reduced pressure and the product finally distilled at 194–196°/0.2 mm.; yield, 181 g. (88%). The diester slowly became a semi-solid at room temperature.

Anal. Calcd. for $C_{26}H_{34}O_4$: C, 76.06; H, 8.35. Found: C, 75.92; H, 8.30.

Hexachlorodiphenyladipic acid. A suspension of 150 g. of diphenyladipic acid (mixed isomers) and 12.8 g. of iodine in 1500 ml. of chloroform was heated to reflux and treated with a rapid stream of chlorine for a period of 5 hr., in the absence of any light. The reaction mixture was filtered to remove any unchanged diphenyladipic acid, and the solvent and catalyst removed by distillation under reduced pressure. The product on cooling to room temperature was an amorphous, glass-like material melting over a broad range beginning at 58°.

Anal. Calcd. for $C_{18}H_{12}O_4Cl_6$: Cl, 42.2%. Found: Cl, 41.4%.

The following observations indicate the product is largely 2,5-dichloro-2,5-bis(3,4-dichlorophenyl)adipic acid: Two of the chlorine atoms in the product were readily removed by refluxing with 10% aqueous caustic, the remaining four chlorines being unaffected. Oxidation of the hexachloro acid with alkaline permanganate yielded 3,4-dichlorobenzoic acid, m.p. 202–204°.

2,5-Diphenylcyclopentanone.[10] A mixture of 233 g. of diphenyladipic acid and 8 g. of finely powdered barium hydroxide was heated under a stream of nitrogen, at 300–320°, until carbon dioxide ceased to be evolved (about 2 hr.). The crude reaction mixture was crystallized first from methanol, then from ethanol to yield 101 g. of product melting at 90.5–91°.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.20; H, 6.78. The filtrate contained 54 g. of an oily product which was not identified.

2,5-Dicyclohexylcyclopentanone. A mixture of 28 g. of 2,5-dicyclohexyladipic acid and 0.1 g. of barium hydroxide was heated at 310–320° for 5 hr., at which time evolution of carbon dioxide ceased. The reaction product was cooled, dissolved in diethyl ether and filtered. The solvent was then evaporated leaving a residue of 20.4 g. (91.5% yield) of almost pure *meso* and racemic ketone. This is a new compound. The higher melting form was separated and purified by crystallization from methanol; m.p. 94–95°.

Anal. Calcd. for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 81.88; H, 11.60.

The original methanolic filtrate yielded a residue which on recrystallization from hexane melted at 41–46°.

Anal. Found: C, 82.35; H, 11.17.

CINCINNATI 37, OHIO

---

(10) P. Ruggli and J. Schmidlin, *Helv. Chim. Acta*, **29**, 396 (1946).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND]

Doubly-Branched Polyphenyls

G. FORREST WOODS, J. E. SWENARTON, AND R. B. ISAACSON

Received May 13, 1960

The synthesis of some doubly-branched polyphenyls, including 1,2,3,5-tetraphenylbenzene, is reported. Melting points and ultraviolet absorption data are tabulated.

The earlier papers[1,2] in this series have dealt with the synthesis, properties, and a mode of nomenclature of linear and singly-branched polyphenyls. It was desired to extend this study into the synthesis and determination of some physical properties of some doubly-branched polyphenyls.

One method that was employed for the synthesis of doubly-branched polyphenyls started with the monomethyl ether of 2,5-diphenyldihydroresorcinol.[3]

---

(1) G. Forrest Woods, D. D. Centola, H. E. Ruskie, and C. David Miller, *J. Am. Chem. Soc.*, **82**, 5227 (1960).

(2) G. F. Woods, J. C. Oppelt, and R. B. Isaacson, *J. Am. Chem. Soc.*, in press.

(3) G. R. Ames and W. Davey, *J. Chem. Soc.*, 3480 (1957).