From the fraction, b. p. 180–190° (2 mm.); $n^{25}\mathrm{D}$ 1.6355, a crystalline crop was secured on trituration with light-petroleum (b. p. 80–100°). After recrystallization from isopropyl alcohol, it formed hexagonal plates, m. p. 110°, and was identical with the hydrocarbon, described by Bergmann and Ukai[7] (m. p. 104–105°). With 2 mols of picric acid in isopropyl alcohol, orange-red needles are formed, which on standing turn into a mixture of dark-red crystals and the colorless plates of the initial hydrocarbon; on further standing, the dark-red crystals disappear too. On heating, the hydrocarbon also dissolves, and when the solution cools down to room temperature, the same effect is reproduced.

The liquid isomer, remaining after the separation of the solid hydrocarbon, was used for the following reactions.

**Reaction with Maleic Anhydride.**—The hydrocarbon (1 g.) and maleic anhydride (0.4 g.) in xylene (10 cc.) were boiled for three hours. On addition of low-boiling light-petroleum, 3,4,6-triphenyl-1,2,3,6-tetrahydrophthalic anhydride (XIII) crystallized. From butyl acetate, needles, m. p. 208–209°; yield 0.3 g. *Anal.* Calcd. for $C_{26}H_{20}O_3$: C, 82.1; H, 5.3. Found: C, 82.6; H, 5.8.

**Reaction with Lithium Metal.**—The reaction was carried out as above; the dark-brown solution, on hydrolysis, gave 1,2,4-triphenylbutene-(2) (XVII) as a colorless, viscous oil, b. p. 140° (0.03 mm.); $n^{19}\mathrm{D}$ 1.5992. *Anal.* Calcd. for $C_{22}H_{20}$: C, 93.0; H, 7.0. Found: C, 92.9; H, 7.0.

## Summary

1. The different reactivities of 1- and 2-vinylnaphthalenes and 2-vinylanthracenes toward maleic anhydride are examined. 2-Isopropenylanthracene shows addition exclusively at the 9,10-double bond.

2. The reactivity of 9-vinylphenanthrenes is compared with the conjugated system of the corresponding α-vinylstilbenes, as regarding the diene reaction and the addition of alkali metals, and the ambiguous character of the 9,10-double bond of phenanthrene is demonstrated.

3. 9-Allylphenanthrene, too, shows the peculiarities of the 9,10-double bond of phenanthrene by the two ways it reacts with lithium.

REHOVOTH, PALESTINE RECEIVED OCTOBER 17, 1939

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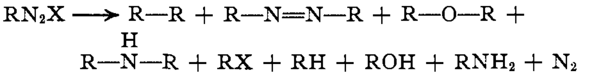
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NEW HAMPSHIRE AND TRINITY COLLEGE (CONN.)]

# A Direct Synthesis of Resolvable Biaryls[1]

BY EDWARD R. ATKINSON AND H. J. LAWLER

It has long been known that diazotized amines decompose in the presence of certain reducing agents to form biaryls along with other products, including the common replacement derivatives, as shown by the generalized equation



$$RN_2X \longrightarrow R{-}R + R{-}N{=}N{-}R + R{-}O{-}R + R{-}\overset{H}{N}{-}R + RX + RH + ROH + RNH_2 + N_2$$

The reaction, which occurs in aqueous solution, invariably leads to symmetrically substituted biaryls[2] and seems to be a genuine reduction; in these respects it differs from the better known Gomberg reaction[3] which is currently being investigated by Waters and others.[4]

The facts concerning the reaction in question may be correlated with respect to (a) the nature of the diazotized amine, (b) the reducing agent used and (c) the experimental conditions which include a number of variables. In an effort to determine the relative importance of these factors and to extend the general applicability of this reaction to matters of synthesis, an extensive study of the reaction has been undertaken.

At the present time it is not possible to state the potential use of the reaction in the synthesis of biaryls and because of this it has not had wide application. However, Vorländer and Meyer,[5] Hunn,[6] and Huntress and his students[7] have used this method for the preparation of diphenic acid and a number of symmetrical substitution products; the preparation of certain binaphthyl dicarboxylic acids from diazotized naphthylamine carboxylic acids has been described in the patent literature.[8]

We have prepared *d,l*-4,6,4′,6′-tetrachlorodiphenic acid (II) and the analogous bromo compound (III) in two steps, starting with the readily available anthranilic acid.

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(1) A preliminary notice of this work was presented at the Rochester meeting of the A. C. S., September, 1937.

(2) The possibility of preparing unsymmetrical biaryls by the use of mixtures of diazotized amines is being investigated.

(3) Gomberg and Bachmann, THIS JOURNAL, **46**, 2339 (1924); Gomberg and Pernert, *ibid.*, **48**, 1372 (1926).

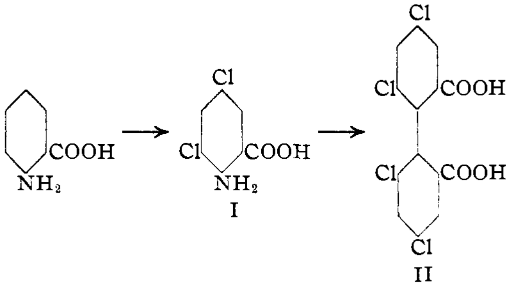
(4) Hey and Waters, *Chem. Rev.*, **21**, 175–183 (1937), and later papers in the *Journal of the Chemical Society* by Waters, Grieve, Hay, Heilbron.

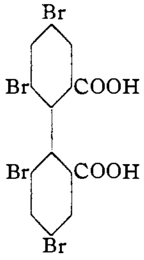
(5) Vorländer and Meyer, *Ann.*, **320**, 122–144 (1902).

(6) Hunn, THIS JOURNAL, **45**, 1024–1030 (1923).

(7) (a) Huntress, "Organic Syntheses," John Wiley and Sons, New York, 1932, Collective Volume I, page 216; (b) THIS JOURNAL, **55**, 2561 (1933); (c) **55**, 4268 and 4270 (1933).

(8) German Patent 445,390, *Friedländer*, **15**, 300 (1928).





III

The halogenation step was thoroughly examined and modifications of published procedures made so as to obtain optimum yields. In the coupling step by using hydrated cuprous oxide and a set of experimental conditions, the development of which will be described in a subsequent paper, we have obtained yields of 50% for the chloro compound and 37% for the bromo compound. Easy recovery of dihalogenoanthranilic acid (I) from the by-products[9] led to net yields of 61 and 53%, respectively. Both the tetrachloro- and tetrabromodiphenic acids were resolved into their active forms by brucine, although no extensive study of optimum resolution procedures was made. These active forms are quite stable to racemization. We now have then a convenient and rapid synthesis of optically active diphenic acids. The use of this class of substances as resolving agents has been discussed by Ingersoll and Little.[10]

Yuan and Hsü[11] have previously described a tetrabromodiphenic acid prepared by the usual Ullmann method from the methyl ester of 3,5-dibromo-2-iodobenzoic acid. Their acid should be identical with ours, yet there are very few points of similarity; even the relative solubility of the two alkaloidal salts is reversed (the same solvent being used). For this reason the rather unexpected easy racemization of the active forms described by these workers may not be significant. As stated above, our active acid was not easily racemized.

## Experimental Part

All melting points reported in this paper were taken by the method described in Mulliken's "Identification of Pure Organic Compounds," Vol. I, page 218, on a 360° rod form melting point thermometer immersed in the sulfuric acid to the 0° point. All melting points are uncorrected.

**3,5-Dichloro-2-aminobenzoic Acid** (I).—Two alternative methods were used for the preparation of this substance.

**Method 1.**—In a typical run based on the method described by Eller and Klemm,[12] 25 g. (0.18 mole) of anthranilic acid was dissolved in 100 cc. of thiophene-free benzene and a solution of 70 g. (0.52 mole) of sulfuryl chloride in 50 cc. of benzene added slowly with cooling and vigorous shaking. The resulting suspension was heated on a water-bath for four hours, cooled, and diluted with one volume of ligroin (b. p. 90–120°). After purification and recrystallization from benzene–alcohol, the light brown product had m. p. 227–230°, weight 19 g. (51% yield); this material was satisfactory for conversion into the tetrachlorodiphenic acid.

**Method 2.**—Direct chlorination of from 10 to 30 g. of anthranilic acid dissolved in glacial acetic acid as described by Elion[13] gave products which could be purified by leaching with boiling benzene until the process no longer removed a red tarry substance. The product had m. p. 223–228°; weight 8.9 g. (59% yield); it was satisfactory for conversion into the tetrachlorodiphenic acid.

Material prepared by either of the above methods could be further purified by recrystallization from benzene–alcohol; white or cream needles, m. p. 230–231°. Elion[13] records m. p. 231°.

***d,l*-4,6,4′,6′-Tetrachlorodiphenic Acid** (II).—The following procedure is that of a typical run. Runs using one-half the amounts described also have been carried out.

Ten grams (0.048 mole) of 3,5-dichloro-2-aminobenzoic acid was dissolved in a mixture of 100 cc. of water and 26 cc. of 2 *N* sodium hydroxide (0.052 mole). To this was added 4 g. (0.056 mole) of sodium nitrite. Mechanical stirring was often necessary to dissolve the latter, since the solution is almost saturated with respect to the sodium salt of the acid. This solution was added in 5-cc. portions with vigorous shaking to a solution of 40 cc. of 6 *N* hydrochloric acid in 20 cc. of water, the latter solution being kept at 0°. The diazotization took place rapidly and the resulting solution was kept at 0° in the dark for about one-half hour, then filtered by suction immediately before use if not entirely clear.

J. T. Baker A. R. grade of cuprous chloride was purified by washing with 1:20 sulfuric acid, then with glacial acetic acid. It was dried at 100° and stored in the dark. Twenty-four grams (0.242 mole) of this pure cuprous chloride was suspended in 200 cc. of water in a 500-cc. round-bottom flask. Forty-two cc. of 6 *N* sodium hydroxide (0.252 mole) was added at about one drop per second while the contents of the flask were vigorously stirred. The resulting orange hydrated cuprous oxide was washed twice with water by decantation, then filtered by suction and sucked as dry as possible. It was transferred mechanically to the flask in which the coupling reaction was to be carried out.

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[9] This material has been shown to be a true by-product and not to result from incomplete diazotization.

[10] Ingersoll and Little, THIS JOURNAL, **56**, 2123 (1934).

[11] Yuan and Hsü, *J. Chinese Chem. Soc.*, **3**, 206 (1935).

[12] Eller and Klemm, *Ber.*, **55**, 222 (1922)

[13] Elion, *Rec. trav. chim.*, **44**, 1106 (1925).

The coupling reaction was carried out in a 500-cc. three-necked round-bottom flask immersed in an ice-bath. The use of a creased flask described by Morton[14] is not recommended. The reducing agent was suspended in a mixture of 30 cc. of ammonium hydroxide (28%) and 40 cc. of water. During the reaction a total of 16 cc. of ammonium hydroxide and 10 cc. of water additional were added from time to time in small portions. The diazonium solution was added at about one drop per second through an addition tube which dipped below the surface of the reducing suspension and then bent upward. The end of this tube was constricted to a diameter of one millimeter. This device prevented premature reaction of the entering diazonium solution with the vapors of the ammoniacal reducing solution. Motor stirring was used and was quite vigorous in the vicinity of the addition tube. Troublesome foaming caused by the vigorous evolution of nitrogen was prevented with a few drops of *n*-butyl alcohol. At the conclusion of addition, excess hydrated cuprous oxide was always present. The solution was brought to a boil and acidified slowly with concentrated hydrochloric acid until acid to congo red; rapid acidification usually gave a tarry product; 50 or 60 cc. additional acid was then added and the crude product which had precipitated was allowed to stand overnight. The crude was filtered off, leached with a cold saturated solution of ammonium chloride at its boiling point to remove copper salts, filtered from the hot solution and washed free of chloride. After drying it had m. p. 177–233°, weight 9 g.

The crude was heated to 150° with 40 cc. of concentrated sulfuric acid and then allowed to cool; if more sulfuric acid was used the entire crude dissolved and the tetrachlorodiphenic acid crystallized out on cooling; normally not all the solid dissolved. The insoluble material was filtered by suction from the sulfuric acid, using a glass filter; it was washed on the filter with cold concentrated sulfuric acid until white, the washings being added to the filtrate (the examination of which is described below). The white solid was then boiled with water to remove residual sulfuric acid and finally filtered and dried; weight, 4.5 g. (49% yield). In some cases the product was recrystallized from ethyl acetate–ligroin. Combinations of alcohol or acetone with water were not suitable because the product invariably separated as an oil. *d,l*-4,6,4′,6′-Tetrachlorodiphenic acid (II) is a white crystalline solid, m. p. 258–259°.

*Anal.* Calcd. for $C_{14}H_6O_4Cl_4$: Cl, 37.4; neut. equiv., 190. Found: Cl, 37.1, 37.1; neut. equiv., 189, 189.

The recrystallization from hot concentrated sulfuric acid confirms the statement of Huntress, Cliff and Atkinson[7c] that diphenic acids containing chlorine atoms in the 6,6′-positions do not undergo fluorenone formation.

In some runs the crude was purified by heating it at 160° and 10 mm. in a sublimation apparatus. The non-sublimable portion was then recrystallized from ethyl acetate–ligroin with use of decolorizing carbon. The product was identical with that obtained above. The yellow sublimate is described below.

**Resolution of *d,l*-4,6,4′,6′-Tetrachlorodiphenic Acid.**—The optical resolution was carried out chiefly as a proof of structure for the substance. All rotations were taken in a 1-dm. semi-micro tube.

Four grams (0.01052 mole) of the acid dissolved in 50 cc. of boiling ethyl acetate was added quickly to a boiling solution of 8.8 g. (0.0223 mole) of anhydrous brucine in 200 cc. of ethyl acetate. A heavy crystalline precipitate appeared. Successive concentrations of the filtrate led to the recovery of 11 g. of salts. Since optical examination of the fractions showed them to be mixtures, they were subjected to a simple fractional crystallization from ethyl alcohol.

The less soluble salt (*l*A·*l*B) had m. p. 264–265°.

*Rotation.* 0.0559 g. made up to 1.95 cc. in chloroform at 24° gave $\alpha_\mathrm{D}$ −0.76; *l*, 1; $[\alpha]^{24}_\mathrm{D}$ −26.5°.

*Anal.* Calcd. for $C_{14}H_6O_4Cl_4\cdot(C_{23}H_{26}O_4N_2)_2$: Cl, 12.16; N, 4.80. Found: Cl, 12.12, 12.12; N, 4.77; 4.84.

The crystalline fraction of the more soluble salt (*d*A·*l*B) having the lowest specific rotation had m. p. 254–259°.

*Rotation.* 0.0519 g. made up to 1.95 cc. in chloroform at 24° gave $\alpha_\mathrm{D}$ −0.21; *l*, 1; $[\alpha]^{24}_\mathrm{D}$ −7.9°.

*Anal.* Calcd. for $C_{14}H_6O_4Cl_4\cdot(C_{23}H_{26}O_4N_2)_2$: N, 4.80. Found: N, 4.61.

During another resolution experiment using aqueous alcohol as solvent and one-half the equivalent amount of brucine, there was isolated the *acid brucine salt of the d-acid*, m. p. 263–265° decompn. after drying at 110°.

*Rotation.* 0.0713 g. made up to 1.95 cc. in chloroform at 25° gave $\alpha_\mathrm{D}$ −0.56; *l*, 1; $[\alpha]^{25}_\mathrm{D}$ −15.3°.

*Anal.* Calcd. for $C_{14}H_6O_4Cl_4\cdot C_{23}H_{26}O_4N_2$: Cl, 18.36; N, 3.62. Found: Cl, 18.1; N, 3.6, 3.7.

***l*-4,6,4′,6′-Tetrachlorodiphenic Acid.**—Two grams of the less soluble salt was decomposed with dilute sodium hydroxide and the liberated brucine removed. The solution was acidified with 6 *N* sulfuric acid and the precipitated *l*-acid recrystallized twice from ethyl acetate–ligroin; m. p. 240–256°.

*Rotation.* 0.0369 g. made up to 1.95 cc. in chloroform at 25° gave $\alpha_\mathrm{D}$ −2.44; *l*, 1; $[\alpha]^{25}_\mathrm{D}$ −129°.

*Anal.* Calcd. for $C_{14}H_6O_4Cl_4$: Cl, 37.4. Found: Cl, 36.9.

***d*-4,6,4′,6′-Tetrachlorodiphenic Acid.**—One gram of the more soluble salt was decomposed as above giving an acid, m. p. 233–250°.

*Rotation.* 0.0308 g. made up to 1.95 cc. in chloroform at 25° gave $\alpha_\mathrm{D}$ +1.99; *l*, 1; $[\alpha]^{25}_\mathrm{D}$ +126°.

By decomposition in a similar manner of the acid brucine salt described above the *d*-acid was obtained, m. p. 252–254°.

*Rotation.* 0.0349 g. made up to 1.95 cc. in chloroform at 25° gave $\alpha_\mathrm{D}$ +2.39; *l*, 1; $[\alpha]^{25}_\mathrm{D}$ +133°.

*Anal.* Calcd. for $C_{14}H_6O_4Cl_4$: Cl, 37.4. Found: Cl, 36.6.

**Examination of By-products.**—From the 9 g. of crude described above there was obtained 4.5 g. of yellow by-products using either the sublimation procedure, where they were obtained as the sublimate, or the sulfuric acid procedure, where they were obtained after pouring the filtrate and washings on crushed ice (water being added to facilitate complete precipitation). The by-products seemed identical with the exception that those obtained by the sulfuric acid method contained a small amount of non-acidic material which after recrystallization from dioxane–water consisted of light yellow needles, m. p. 244–249°,

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[14] Morton, *Ind. Eng. Chem., Anal. Ed.*, **11**, 170 (1939).

containing 3.9% nitrogen and 38.7% chlorine. This material showed a strong green fluorescence in concentrated sulfuric acid or in alcohol. This fluorescence was quenched by the addition of acid to the alcohol solution. The aqueous dioxane filtrate gradually decomposed as it evaporated, giving a brown tarry solid with a charred odor. Neither this nor the yellow crystalline material was examined further. After elimination of this non-acidic material the by-products were recrystallized from benzene–alcohol. The first fraction consisted of pale yellow needles, m. p. 230–231°, weight 1.2 g.; this did not depress the melting point of authentic 3,5-dichloro-2-aminobenzoic acid. An additional 1.1 g. of material of m. p. 219–229° was obtained by concentration of the filtrate. The residues melted at still lower temperatures and were not examined. They probably contained 2,3,5-trichlorobenzoic acid for this substance had been isolated in earlier runs where the crude was leached with boiling water; it crystallized from the hot water in white needles, m. p. 161–163°. Cohen and Dakin[15] record m. p. 162°.

*Anal.* Calcd. for $C_7H_3O_2Cl_3$: Cl, 47.3. Found: Cl, 46.3.

The 2.3 g. of material recovered actually contained 2 g. of 3,5-dichloro-2-aminobenzoic acid; this was shown by using the material along with similar material from other runs as starting material for a normal coupling run. Only 10% failed to diazotize and the yield of tetrachlorodiphenic acid was normal.

If correction is made for the 2 g. of starting material recovered in usable form, the net yield of tetrachlorodiphenic acid is raised to 61%.

The 3,5-dichloro-2-aminobenzoic acid recovered seems to be a true by-product; it does not result from incomplete diazotization. First, it is insoluble in acids of a concentration existing in the diazonium solution and the latter had been filtered before use. Second, a quantitative analysis of a typical diazonium solution prior to use, based on the coupling reaction with $\beta$-naphthol and using the salt pile indicator technique, showed complete diazotization.

**3,5-Dibromo-2-aminobenzoic Acid.**—Twenty grams of anthranilic acid was brominated following the procedure of Wheeler and Oates[16] with minor variations. The crude acid was obtained in yields of about 80% and was suitable for conversion to the tetrabromodiphenic acid. By recrystallization from alcohol–water it was obtained in 60% yields, m. p. 232–233°. Wheeler and Oates[16] record 232°.

*Anal.* Calcd. for $C_7H_5O_2NBr_2$: Br, 54.2; N, 4.75; neut. equiv., 295. Found: Br, 54.4; N, 4.93; neut. equiv., 296.

***d,l*-4,6,4′,6′-Tetrabromodiphenic Acid.**—Ten grams (0.034 mole) of 3,5-dibromo-2-aminobenzoic acid and 3 g. (0.042 mole) of sodium nitrite were dissolved in 185 cc. of water and 20 cc. of 2 *N* sodium hydroxide (0.04 mole). The diazotization was carried out as for the analogous chloro acid using 30 cc. of 6 *N* hydrochloric acid and 20 cc. of water. The reducing agent was prepared from 17 g. of purified cuprous chloride. The coupling suspension contained 24 cc. of ammonium hydroxide (28%) and 36 cc. of water. During the reaction an additional 12 cc. of ammonium hydroxide and 10 cc. of water was added. The manipulative technique was the same as that described above for the chloro acid.

The crude was purified by either the sublimation or concentrated sulfuric acid procedures. Using the latter there was obtained 3.5 g. (37% yield) of the white crystalline product, m. p. 303–306°. Recrystallization from ethyl acetate–ligroin gave a slightly purer product, m. p. 305–308°.

*Anal.* Calcd. for $C_{14}H_6O_4Br_4$: Br, 57.3; neut. equiv., 279. Found: Br, 57.1, 57.2; neut. equiv., 279, 279.

The by-products obtained by either purification procedure were treated as described for the chloro acid. From these in the run just described there was obtained 1.2 g. of pure 3,5-dibromo-2-aminobenzoic acid, m. p. 230–233°. Moreover, the total amount of such material recovered in usable form was 3 g. The net yield of tetrabromodiphenic acid is then raised to 53%.

**Resolution of *d,l*-4,6,4′,6′-Tetrabromodiphenic Acid.**—Five grams (0.009 mole) of the acid in 70 cc. of hot ethyl acetate was added quickly to a solution of 8 g. (0.0203 mole) of anhydrous brucine in 200 cc. of boiling ethyl acetate. In a few minutes 6.2 g. of salt separated from the boiling solution. This less soluble salt (*l*A·*l*B) was leached with 400 cc. of boiling anhydrous ethyl alcohol. The residue and the first solid obtained on cooling the alcohol had about the same rotation and m. p. 259–260° decompn.

*Rotation.* 0.0350 g. made up to 1.95 cc. chloroform at 24° gave $\alpha_D$ −0.19; *l*, 1; $[\alpha]^{24}_D$ −10.6°.

*Anal.* Calcd. for $C_{14}H_6O_4Br_4{\cdot}(C_{23}H_{26}O_4N_2)_2$: N, 4.16; Cl, 23.7. Found: N, 4.54; Cl, 23.2.

The more soluble salt (*d*A·*l*B) was obtained only when the original ethyl acetate solution had been concentrated to 50 cc.; 1.8 g. so obtained was crystalline but even after drying for five hours at 80° and 5 mm. it had m. p. 123–204° decompn.

*Rotation.* 0.0333 g. made up to 1.95 cc. in chloroform at 25° gave $\alpha_D$ −0.55; *l*, 1; $[\alpha]^{25}_D$ −32.2°.

*Anal.* Calcd. for $C_{14}H_6O_4Br_4{\cdot}(C_{23}H_{26}O_4N_2)_2$: N, 4.16; Found: N, 4.10.

There was also a considerable amount of glassy residue which when decomposed gave the *d*-acid with a rotation slightly greater than that given by the acid from the crystalline fraction of the more soluble salt.

***l*-4,6,4′,6′-Tetrabromodiphenic Acid.**—The less soluble salt was decomposed with dilute sodium hydroxide giving an acid which upon recrystallization from ethyl acetate–ligroin had m. p. 282–283°.

*Rotation.* 0.1319 g. made up to 1.95 cc. in anhydrous ethyl alcohol[17] at 25° gave $\alpha_D$ −0.52; *l*, 1; $[\alpha]^{25}_D$ −7.7°.

*Anal.* Calcd. for $C_{14}H_6O_4Br_4$: Br, 57.3. Found: Br, 57.1.

***d*-4,6,4′,6′-Tetrabromodiphenic Acid.**—The glassy residue was decomposed as above to give an acid which after recrystallization from ethyl acetate–ligroin had m. p. 279–282°.

*Rotation.* 0.0583 g. made up to 1.95 cc. in anhydrous ethyl alcohol at 25° gave $\alpha_D$ +0.20; *l*, 1; $[\alpha]^{25}_D$ +6.7°.

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[15] Cohen and Dakin, *J. Chem. Soc.*, **81**, 1331 (1902).

[16] Wheeler and Oates, THIS JOURNAL, **32**, 770 (1910).

[17] This solvent was used for the bromo acids because of their very low solubility in chloroform.

*Anal.* Calcd. for $C_{14}H_6O_4Br_4$: Br, 57.3. Found: Br, 57.4.

**Racemization Experiments.**—A sample of *l*-4,6,4′,6′-tetrachlorodiphenic acid having $[\alpha]_D$ −129° (in chloroform) was refluxed in a 1 *N* sodium hydroxide solution for six hours. It was recovered by acidification and dried. It then showed $[\alpha]_D$ −126°. The decrease is probably not significant.

A sample of *d*-4,6,4′,6′-tetrabromodiphenic acid having $[\alpha]_D$ +6.7° (in alcohol) was dissolved in a 1 *N* sodium hydroxide solution and kept at 80° for five days. It was recovered by acidification and had the same rotation.

## Summary

1. The biaryl synthesis involving the action of reducing agents on aqueous solutions of diazotized amines has been applied to the synthesis of resolvable diphenic acids. The method constitutes a rapid and direct synthesis of these substances.

2. *d,l*-4,6,4′,6′-Tetrachlorodiphenic acid and the analogous tetrabromodiphenic acid have been prepared by this method in one step from the appropriate 3,5-dihalogeno-2-aminobenzoic acids. Net yields obtained were 61 and 53%, respectively. The acids were resolved into their active forms by means of brucine.

DURHAM, N. H. RECEIVED APRIL 24, 1940

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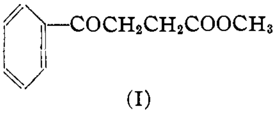
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# Polymethyl Aromatic Hydrocarbons. I. Synthesis of 1,2,4-Trimethylnaphthalene and 1,2-, 1,3- and 1,4-Dimethylnaphthalene

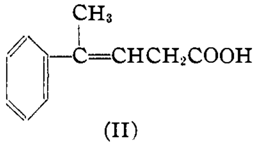
BY M. C. KLOETZEL

Research now in progress required the preparation of certain di- and tri-methylnaphthalenes in sizable quantity and free from isomers. Herein is described the synthesis of 1,2,4-trimethylnaphthalene (XVI) and 1,2-, 1,3- and 1,4-dimethylnaphthalene by new methods which fulfil these requirements.

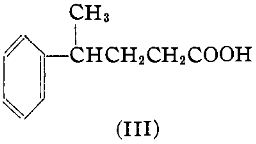
The readily available β-benzoylpropionic acid was utilized as the starting material for the preparation of 4-methyl-1-tetralone (IV) and from this cyclic ketone in turn were synthesized 1,3- and 1,4-dimethylnaphthalene and 1,2,4-trimethylnaphthalene (XVI). When methyl β-benzoylpropionate (I) was treated with methylmagnesium iodide 4-phenylpenten-3-oic acid (II) was produced. This acid has been prepared previously by Mayer and Stamm[1] but in only 26% yield. It was therefore of primary importance that this step in the synthetic scheme be improved. Consistent 70–75% yields of 4-phenylpenten-3-oic acid (II) finally were afforded by means of strict adherence to certain precautions, notably the use of 1.38 moles of methylmagnesium iodide per mole of methyl β-benzoylpropionate, and maintenance of the reaction temperature near 0° during addition of the Grignard reagent. An acetic acid solution of (II) rapidly absorbed hydrogen in the presence of Adams catalyst to give a quantitative yield of 4-phenylpentanoic acid (III). Inasmuch as the cyclization of 4-phenylpentanoyl chloride with aluminum chloride has been reported[1,2] to give (IV) in yields of 70–75%, the simpler direct cyclization of the acid (III) with 80% sulfuric acid was employed and the desired cyclic ketone (IV) was obtained thereby in 74% yield.



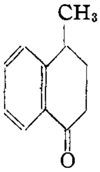
(I)



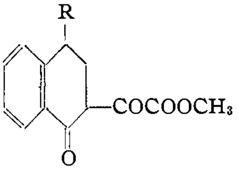
(II)



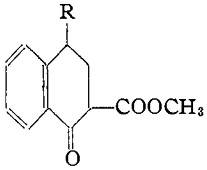
(III)



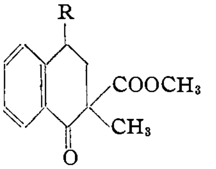
(IV)



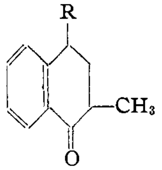
(V, R = CH₃)
(XVII, R = H)



(VI, R = CH₃)
(XVIII, R = H)



(VII, R = CH₃)
(XIX, R = H)



(VIII, R = CH₃)
(XX, R = H)

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(1) Mayer and Stamm, *Ber.*, **56**, 1424 (1923).

(2) Von Braun and Stuckenschmidt, *ibid.*, **56**, 1724 (1923).