Palladium-Catalyzed Syntheses of Aromatic Coupling Compounds

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The oxidative coupling of aromatic compounds is catalytic under oxygen pressure in the presence of palladium acetate. The addition of acetylacetone or EDTA to the system remarkably promoted the yield of coupling products, whereas acids, bases, lithium chloride, polar solvent, and certain metal ions inhibited the reaction. The steric and polar effects of substituents were also observed in the coupling reaction. The procedure described in this publication would provide a convenient method for preparation of biphenyltetracarboxylic acids from *o*-xylene, dimethyl phthalate, and naphthalene. The separation of the isomers was achieved by recrystallization.

Palladium on charcoal is generally known to be a highly effective catalyst for dehydrogenation of hydrocarbons, but not for the coupling reaction of aromatic compounds. The conversion of *o*-terphenyl to triphenylene[1] is one of the examples of a dehydrogenation reaction. In 1965, Helden and Verberg[2] reported the coupling of benzene in acetic acid in the presence of palladium chloride and sodium acetate. They also found that no reaction occurred without sodium acetate and the yield of biphenyl was low because palladium metal was precipitated during the reaction. In subsequent studies by Davidson and Triggs,[3] a profound effect of molecular oxygen upon the reactivity of palladium acetate was found, by which the acetoxylation was almost completely inhibited and biphenyl was mainly produced. They also stated a possibility of catalytic oxidative coupling under 50 atm pressure of oxygen since palladium was retained in the solution without cocatalyst ions. In our earlier work,[4] we found that the coupling reactions between aromatic compounds and olefins were catalyzed by oxygen with the pressure higher than 3 kg/cm^2. Also, we later observed[5] that aromatic coupling compounds were obtained in high yields in the absence of acetic acid by using palladium acetate as a catalyst.

In an extention of our research on the coupling reaction, the effect of oxygen pressure on the coupling of toluene was examined under various pressures of a gaseous mixture of nitrogen and oxygen (molar ratio of 1:1). Table I shows that the yields of bitolyl increase with increasing oxygen pressure. If the pressure is higher than 50 kg/cm^2, the yield does not remarkably increase. Therefore, further experiments were designated to be carried out under 50 kg/cm^2 of the gaseous mixture. Although oxygen can be used in the pure state, it is preferable, for prevention of explosions, to use a gaseous mixture of oxygen and an inert gas such as nitrogen or a rare gas. In addition, special care must be taken not to use excess cumene, anisole, tetralin, 1-butanol, or sulfuric acid. Otherwise, an explosion may occur during the reaction.

TABLE I

EFFECT OF THE PRESSURE OF A GASEOUS MIXTURE OF N_2 AND O_2 (1:1) ON THE YIELD OF BITOLYL[a]

Pressure,[b] kg/cm^2	Yield of bitolyl, %[c]
6	110
12.5	500
25	760
50	1800
75	1800

[a] Toluene (50 ml), Pd acetate (0.5 mmol), 120°, 4 hr. [b] Pressure filled at room temperature before reaction. [c] Based on Pd acetate used.

The effect of the additives on the coupling of dimethyl phthalate is shown in Table II. By adding an equimolar amount of acetylacetone to palladium acetate, the yield of coupling products is greatly improved. In a stainless steel vessel where certain metal ions such as iron, nickel, and chromium ions may be contaminated in the reaction medium, the coupling reaction is remarkably suppressed. However, the yields of coupling products are increased by addition of ethylenediaminetetraacetic acid. This effect is probably due to the formation of inactive complexes between ethylenediaminetetraacetic acid and certain metal ions. We have also found that by the addition of hydrochloric acid, sulfuric acid, sodium acetate, triphenylphosphine, bipyridyl, pyridine, lithium chloride, cyclooctadiene, and certain metal ions to the reaction mixture, or using a polar solvent such as dimethylformamide or acetonitrile, the yield of coupling products was extremely small or none at all. Catalytic activity of palladium acetate decreased gradually during the reaction, since water is formed.

TABLE II

EFFECT OF ACETYLACETONE OR EDTA ON THE COUPLING OF DIMETHYL PHTHALATE

Dimethyl phthalate, mmol	300[b]		100[c]	
Pd acetate, mmol	3		1	
	In glass[d]	In stainless[e]	In glass[d]	In stainless[e]
Blank	4600	1700	2100	1900
Acac	6900	8000	5000	5200
EDTA[a]		4400		2800
Acac + EDTA		4400		

[a] EDTA stands for ethylenediaminetetraacetic acid. [b] The autoclave of 1-l. capacity, acetylacetone (3 mmol), EDTA (3 mmol), 150°, 23 hr. [c] The autoclave of 300-ml capacity, acetylacetone (1 mmol), EDTA (1 mmol), 150°, 6 hr. [d] The reaction was carried out in a glass vessel. [e] The reaction was carried out without a glass vessel.

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(1) P. G. Copeland, R. E. Dean, and D. McNeil, *J. Chem. Soc.*, 1687 (1960).

(2) R. van Helden and G. Verberg, *Recl. Trav. Chim. Pays-Bas*, **84**, 1263 (1965).

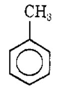
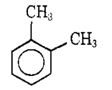
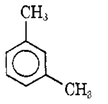
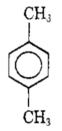
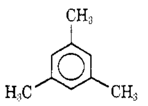
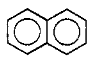
(3) J. M. Davidson and G. Triggs, *Chem. Ind. (London)*, 457 (1966); 1361 (1967); *J. Chem. Soc. A*, 1324, 1331 (1968).

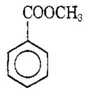
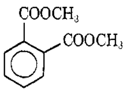
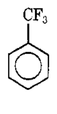
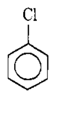
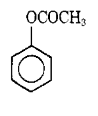
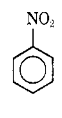
(4) (a) Japanese Patent Application No. 92041 (1968). (b) Symposium of Homogeneous Catalytic Reactions Involving Palladium, American Chemical Society, Minneapolis, Minn., April 13-18, 1969, p 172.

(5) H. Itatani and Y. Yoshimoto, *Chem. Ind. (London)*, 674 (1971).

TABLE III

COUPLING OF AROMATIC COMPOUNDS (50 ml) WITH PALLADIUM ACETATE (0.5 MMOL) AND ACETYLACETONE (0.5 MMOL) AT 150° FOR 4 HR

Compd							
Yield,^{a}%	3100	7400	5700	4100	400	0	4500

Compd							
Yield,^{a}%	8500	5200	700	400	2300	5700	2500

[a] Mole per cent yield based on palladium acetate used, but the possible isomers were not separated for analysis.

Coupling of toluene gives bitolyl in 20,600% yield based on palladium acetate used, indicating reoxidation of reduced palladium. Bitolyls formed consisted of six isomers, the composition of which is reaction temperature dependent. From the composition of bitolyl formed, the relative reactivities of ortho to meta and para to meta can be calculated to be 0.27 and 0.70 in palladium-catalyzed coupling of toluene, and 0.07 and 0.61 in aluminum-catalyzed isomerization of 4,4′-dimethylbiphenyl. These facts indicate that both reactions are favored meta and para substitutions. The system of mercury acetate and palladium acetate[6] shows the relative reactivities of ortho to meta and para to meta as 0.29 and 3.04, indicating preferable para substitution.

Table III shows the yield of the coupling products of substituted benzenes. The coupling products of methyl-substituted benzenes decrease in the order toluene > *o*-xylene > *m*-xylene > *p*-xylene, probably owing to the steric effect of the methyl group. No coupling occurs in the case of mesitylene, which has two methyl groups ortho to a hydrogen on benzene nucleus. Halogenated benzenes give low yields of coupling products, since the presence of halogen causes precipitation of palladium black during the reaction. No coupling product could be obtained under the present reaction conditions from aromatic compounds containing amino, cyano, and acid anhydride groups. Phenyl acetate and methyl benzoate give high yields of coupling products with a small amount of by-products.

Coupling of *o*-xylene gives mainly 3,4,3′,4′-tetramethylbiphenyl, while the coupling of dimethyl phthalate gives tetramethyl 2,3,3′,4′- and 3,4,3′,4′-biphenyltetracarboxylates. The coupling of naphthalene gives 43% of α,α'-, 50% of α,β'-, and 7% of β,β'-binaphthyls. There is a drastic change in the isomer distribution of the coupling products. *o*-Xylene is preferably converted to β isomers whereas naphthalene is converted to α isomers. This may be rationalized by assuming that the former is controlled mainly by steric requirements of the methyl group while the latter is influenced by a polar effect depending on self-polarizability at the α position of naphthalene.

For understanding the present results, we consider the reaction process. Helden and Verberg[2] first considered a coupling process *via* $\sigma-\pi$ palladium complex. Later, Davidson and Triggs[3] proposed an intermolecular coupling through σ-phenyl palladium(II) complex which was reduced partially to palladium(I). On the basis of isomer distributions affected by substituents, an intramolecular coupling of σ-diaryl palladium(II) complexes[6] has been postulated. In the present study, however, the reaction process is catalytic under oxygen pressure in the absence of acetic acid. Although discussion in detail concerning a reaction mechanism will be described in a subsequent publication, the overall reaction in the formal way can be expressed as follows.

$$2RH + Pd^{2+} \longrightarrow RPdR + 2H^+$$

$$RPdR \longrightarrow RR + Pd$$

$$RH + Pd + O_2 \longrightarrow RPdOOH$$

$$RPdOOH + RH \longrightarrow RPdR + HOOH$$

$$RPdR \longrightarrow RR + Pd$$

Palladium(0) complex formed can be reoxidized to σ-phenyl palladium(II) hydrogen peroxide by molecular oxygen under pressure, and thus the coupling reaction can be cycled. A similar mechanism[7] has been postulated in the cumene autoxidation catalyzed by oxygen-coordinated palladium complex. The formation of cresol and benzoic acid with bitolyl may be explained by the reactions of toluene and hydroxy radical which would be formed by the decomposition of hydrogen peroxide.

The palladium-catalyzed coupling is highly applicable to the organic syntheses of biphenyltetracarboxylic acid and its dianhydride, which have hitherto been prepared only by cumbersome multistep syntheses. In addition, a new compound, tetramethyl 2,3,3′,4′-biphenyltetracarboxylate, was obtained in the coupling of dimethyl phthalate. Figure 1 shows the characteristic nmr spectrum, different from those of known isomeric tetramethyl biphenyltetracarboxylates. Attempts to separate the two isomeric esters were unsuccessful either by fractional distillation or recrystallization. After hydrolysis of the esters, how-

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[6] M. O. Unger and R. A. Fouty, *J. Org. Chem.*, **34**, 18 (1969). The sum of the mole per cent of isomers at 90° is written to be 110.9. This raises the question.

[7] E. W. Stern, "Homogeneous Metal Catalyzed Oxidation of Organic Compounds, Transition Metals in Homogeneous Catalysis," Marcel Dekker, New York, N. Y., 1971, p 140.

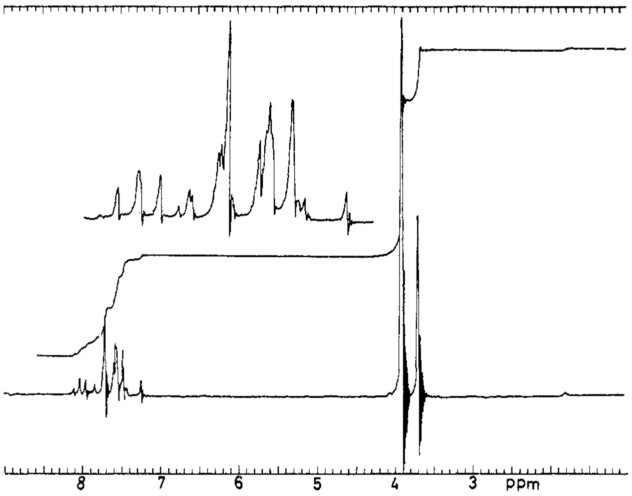

Figure 1.—Nmr of tetramethyl 2,3,3′,4′-biphenyltetracarboxylate in $CDCl_3$.

ever, a mixture of 2,3,3′,4′- and 3,4,3′,4′-biphenyltetracarboxylic acids was able to be separated by recrystallization from water owing to marked differences in the solubility of the two acids. A mixture of acid dianhydrides was also separated by recrystallization from acetic anhydride or acetone.

Finally it is worth noticing that from the product distribution due to substituents, 3,4,3′,4′-biphenyltetracarboxylic acid can be conveniently produced from *o*-xylene or dimethyl phthalate as starting material, while the 2,3,3′,4′-isomeric acid can be produced from dimethyl phthalate or naphthalene, and the 2,3,-2′,3′-isomeric acid can be produced from naphthalene, respectively. Biphenyltetracarboxylic acid dianhydrides obtained from their tetracarboxylic acids have chemical properties similar to those of pyromellitic acid dianhydride, which has been applied in various commercial fields.

Experimental Section[8]

1.—All chemicals were reagent grade and used without further purification. Benzene, toluene, and *o*-xylene were purified by distillation and dried over sodium ribbons. Palladium acetate was prepared according to the literature.[9]

The products separated were identified by elemental analysis, ir, nmr, and mass spectra. The coupling products listed in Table III were identified by a combination of gas chromatographic separation and analysis by mass spectrometry, but the possible isomers were not separated.

Unless otherwise indicated, all reactions were carried out in an autoclave which contained a glass vessel bored with a pin hole. A gaseous mixture of oxygen and nitrogen in the molar ratio of 1:1 was introduced into an autoclave until the inner pressure reached 50 kg/cm^2 at room temperature. The autoclave was shaken (35 times/min) and the temperature was elevated. After the reaction, the solution was analyzed by glc using both a 2-m stainless steel column packed with 5% Apiezon L on Diasolid and a 1-m column with 20% SE-30 using helium as carrier gas. For the determination of yields, the following internal standards were used: dibenzyl for the coupling of benzene, *o*-xylene, mesitylene, and chlorobenzene; stilbene for *p*-xylene and methyl benzoate; 3,5-diisopropyltoluene for trifluoromethylbenzene; pyrene or α,α'-binaphthyl for dimethyl phthalate; triphenylethylene for naphthalene.

2. **Coupling of Toluene.**—A mixture of palladium acetate (0.224 g, 1 mmol), acetylacetone (0.20 g, 2 mmol), and toluene (300 ml) was shaken at 160° for 5 hr under 65 kg/cm^2 of the gaseous mixture. The reaction mixture was concentrated on an oil bath at 130°, precipitates being separated from it. The filtrate was distilled at 105–125° (2 mm) to give 37.38 g of bitolyl (20,600% based on palladium acetate). The ratio of six bitolyl isomers was determined by glc (Apiezon, 170°) and the result showed as following: 2% of 2,2′-, 13% of 2,3′-, 10% of 2,4′-, 27% of 3,3′-, 35% of 3,4′-, and 13% of 4,4′-bitolyls. The products obtained were characterized by comparison of glc retention time with that of an authentic specimen.[10] The residue remaining in the flask was extracted with aqueous sodium hydrogen carbonate, giving sodium benzoate. Extraction of the residue with aqueous potassium hydroxide afforded the sodium salt of cresols, which structures were identified by comparison of their ir and glc retention times with those of authentic samples.

3. **Separation of 4,4′-Dimethylbiphenyl.**—To the mixture of bitolyls (50 g) was added a few milligrams of 4,4′-dimethylbiphenyl, and then the mixture was cooled in a Dry Ice–acetone bath with vigorous stirring. The mixture became viscous, and crystals precipitated out. On standing at the temperature of −12° overnight, crystals precipitated and were filtered quickly, giving 0.97 g (15%) of 4,4′-dimethylbiphenyl, mp 120–121°.

Anhydrous aluminum chloride (1.33 g, 10 mmol) and toluene (50 ml) were added to the filtrate. After heating and stirring at 120° for 10 hr, the reaction mixture was diluted with ice water (100 ml) and then extracted with toluene (3 × 50 ml). The toluene was distilled off from the extracts to give dimethylbiphenyls (38.2 g) which were then worked up with aluminum chloride as described in the above procedure; 2.2 g (40%) of 4,4′-dimethylbiphenyl was thus isolated.

4. **Isomerization of Bitolyl with Aluminum Chloride.**—Isomerization of 4,4′-dimethylbiphenyl (1 mmol) with aluminum chloride (0.1 mmol) in toluene (2 ml) was carried out at 120°. The isomer distribution of bitolyls approached a constant after 3 hr. Similarly, bitolyls (10 mmol) obtained by palladium catalysis (expt 2) were isomerized with aluminum chloride, resulting in the same distribution as that obtained from 4,4′-dimethylbiphenyl. Bitolyls in equilibrium consist of 1% of 2,2′-, 2% of 2,3′-, 4% of 2,4′-, 36% of 3,3′-, 39% of 3,4′-, and 14% of 4,4′-dimethylbiphenyls. The remains contain phenyltolylmethane and a slight amount of dibenzyl.

5. **Coupling of *o*-Xylene.**—In a 1-l. capacity autoclave, *o*-xylene (300 ml) and palladium acetate (0.672 g, 3 mmol) were shaken at 150° for 5 hr under 65 kg/cm^2 of the gaseous mixture. After the mixture had cooled to room temperature, the autoclave was degassed and refilled with 50 kg/cm^2 of hydrogen, then allowed to stand overnight. Palladium black (0.31 g, 97%) precipitated and was filtered off, washed with water, and dried. *o*-Xylene was removed by distillation from the filtrate and subsequently the fraction boiling between 148 and 167° (4 mm) was collected. The yield of bixylyl is 32.8 g (5200% based on Pd acetate). Glc (20% SE, 180°) analysis showed the isomer distribution of 1% of 2,3,2′,3′-, 24% of 2,3,3′,4′- and 75% of 3,4,3′,4′-tetramethylbiphenyls. The distillation residue was black tarry solid (33.1 g) which was dissolved in acetone and precipitated by addition of methanol. High-resolution mass spectrometry[11] showed that the residues contained coupling dimers, trimers, and tetramers of *o*-xylene, 2-methylbenzaldehyde, 2-methylbenzoic acid, and also their coupling products. The distilled bixylyl (32.8 g) was recrystallized from methanol (80 ml) to give 13.5 g of pure 3,4,3′,4′-tetramethylbiphenyl whose ir, nmr, and mass spectra were identical with those of an

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(8) Melting points measured were uncorrected. Infrared spectra were recorded using a Hitachi EP 1-G2 spectrophotometer. A JNM-C-60 HL was used for nmr measurement with tetramethylsilane as internal standard. Mass spectra were obtained by a Hitachi RMU-6 and gas chromatographic analyses were performed by a Shimazu GC 4-APT gas chromatograph.

(9) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3636 (1965).

(10) 3,3′-Dimethylbiphenyl boiling at 125–129° (3 mm) was prepared from *o*-tolidine according to the literature ("Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 295). 2,2′-Dimethylbiphenyl boiling at 110–114° (3 mm) was synthesized by the procedure reported [M. S. Kharasch and E. K. Fields, *J. Amer. Chem. Soc.*, **63**, 2319 (1941)] using 2-bromotoluene as starting material. By the same manner, 4-bromotoluene was converted to 4,4′-dimethylbiphenyl, mp 121–122° (recrystallized from ethanol). The coupling reaction between 3-methylcyclohexanone and 4-methylphenylmagnesium bromide was carried out by the modified procedure [M. Orchin, *J. Amer. Chem. Soc.*, **68**, 571 (1946)], followed by dehydrogenation with sulfur to give 3,4′-dimethylbiphenyl boiling at 134–136° (6 mm). By the same procedure, 2,3′- [bp 104–106° (4 mm)] and 2,4′-dimethylbiphenyl [bp 101–103° (3 mm)] were prepared from the reactions of 2-methylphenylmagnesium bromide with 3- and 4-methylcyclohexanones, respectively.

(11) A JEOL, JM S-01SG-2 mass spectrometer was employed.

authentic sample. The mixture melting point with an authentic sample showed no depression.

6. **Coupling of Dimethyl Phthalate to Tetramethyl Biphenyltetracarboxylate (TMBT).**—Dimethyl phthalate (2.5 l., 3 kg), palladium acetate (3.36 g, 0.015 mol), and acetylacetone (1.50 g, 0.015 mol) were placed into an electromagnetically agitating typed stainless autoclave (5-l. capacity) equipped with a sampling tube. The autoclave under 50 kg/cm^2 pressure of the gaseous mixture was stirred (500 rpm) and heated in an oil bath at 130–134° for 1 hr, 130–150° for 1 hr, and then at the constant temperature of 150° for 12 hr. The temperature of the oil bath should be carefully elevated since the reaction was exothermic. During the reaction, the reaction mixture (200 g) was withdrawn periodically for glc (20% SE, 260°). After reaction, the autoclave was cooled to room temperature, degassed, and refilled to 50 kg/cm^2 of hydrogen and then allowed to stand overnight. Palladium black (1.55 g, 97%) precipitated and was removed by filtration and washed with water. The combined filtrates were concentrated on an oil bath (below 200°) under reduced pressure (3 mm) to remove a mixture of water and low-boiling products (37 g) and also dimethyl phthalate (2140 g). The residue (I, 594 g) was recrystallized from 1 l. of methanol to give 120 g of white crystals (II). From the mother liquor, white crystals (III, 10 g) were collected. Distillation of methanol gave the residue, which was distilled on a salt bath under reduced pressure. The fraction (IV, 306 g) boiling at 200–280° (1 mm) and tarry residue (105 g) were collected. The total yield of crude tetramethyl biphenyltetracarboxylate (II + III + IV) was 436 g (7250% based on Pd acetate). Fraction IV was treated with charcoal in methanol (200 ml). The charcoal was filtered off and washed with hot methanol (100 ml). On cooling the combined solution, crystals (V, 219 g) were collected.

The fractional distillation of 140 g of the product V afforded the following fractions: 1st fraction, bp 184–242° (1 mm), 77.6 g; 2nd fraction, bp 242–252° (1 mm), 27.0 g; 3rd fraction, bp 253–260° (1 mm), 25.2 g; the residue, 11.7 g. Each fraction was recrystallized from 100, 30, 40, and 30 ml of methanol, respectively, to give white crystals of VI (66.4 g), VII (23.6 g), VIII (20.7 g), and IX (2.0 g). Glc analysis of the marked compounds shows the compositions of 2,3,2′,3′-, 2,3,3′,4′-, and 3,4,3′,4′-TMBT as 3, 57, 40 for I; 0, 97, 3 for II; 1, 46, 53 for V; 0, 60, 40 for VI; 0, 38, 62 for VII; 0, 5, 95 for VIII; and 0, 11, 89 for IX, respectively.

7. **Identification of TMBT.** A.—The crystals II were treated with charcoal and recrystallized from methanol to give 2,3,3′,4′-TMBT: mp 109–111°; nmr ($CDCl_3$) δ 3.70 (s, 3, 2-$COOCH_3$), 3.91 (s, 9, 3,3′,4′-$COOCH_3$), 7.50–7.55 (m, 3, 5,6,6′-H), 7.72 (s, 1, 2′-H), 7.75–7.85 (d, 1, 5′-H), 7.96–8.12 (t, 1, 4-H); ir (KBr) 3000 (w), 2950 (w), 1720 (s), 1420 (s), 1280 (s), 1200 (m), 1160 (m), 1120 (m), 1080 (w), 1060 (m), 960 (m), 920 (w), 860 (w), 820 (m), 795 (w), 780 (m), 760 (w), 750 (m), 700 (m), 680 cm^{-1} (w).

Anal. Calcd for $C_{20}H_{18}O_8$: C, 62.17; H, 4.70. Found: C, 62.29; H, 4.87.

B.—The compound VIII was recrystallized from methanol to give 3,4,3′,4′-TMBT: mp 105–106° (lit.[12] mp 99–100°); nmr ($CDCl_3$) δ 3.93 (s, 12, 3,4,3′,4′-$COOCH_3$), 7.84 (s, 2, 2,2′-H), 7.88 (d, 2, J = 6 Hz, 6,6′-H), 7.90 (d, 2, J = 6 Hz, 5,5′-H); ir (KBr) 2950 (m), 1720 (s), 1600 (m), 1430 (s), 1280 (s), 1190 (m), 1160 (m), 1120 (m), 1080 (m), 1040 (w), 950 (m), 890 (w), 840 (m), 820 (m), 780 (m), 760 (m), 700 cm^{-1} (w).

Anal. Calcd for $C_{20}H_{18}O_8$: C, 62.17; H, 4.70. Found: C, 62.20; H, 4.80.

C. **Preparation of 2,3,2′,3′-TMBT.**[13]—This compound showed nmr ($CDCl_3$) δ 3.60 (s, 6, 2,2′-$COOCH_3$), 3.91 (s, 6, 3,3′-$COOCH_3$), 7.35–7.54 (d, 4, 5,5′, 6,6′-H), 7.93–8.10 (t, 2, 4,4′-H).

Anal. Calcd for $C_{20}H_{18}O_8$: C, 62.17; H, 4.70. Found: C, 62.41; H, 4.62.

8. **Preparation of Biphenyltetracarboxylic Acid Dianhydride (BTDA).** A.—The crystals V (10 g), water (25 ml), acetic acid (25 ml), and sulfuric acid (5 ml) were refluxed for 6 hr. On cooling, the crystals formed were filtered, washed with water, and dried, giving 4.4 g (51.4%) of 3,4,3′,4′-biphenyltetracarboxylic acid, mp 295–302,° which was then esterified with methanol and sulfuric acid to tetramethyl ester. Glc analysis of the ester showed a single peak.

Concentration of the filtrate gave crystals, which were collected and recrystallized from hot water to afford 3.7 g (43.3%) of 2,3,3′,4′-biphenyltetracarboxylic acid, mp 193–204°. After esterification with methanol and sulfuric acid, the ester showed a single peak in glc analysis.

B.—2,3,3′,4′-TMBT (65 g), sulfuric acid (30 ml), acetic acid (160 ml), and water (160 ml) were refluxed for 5 hr. On concentrating the reaction mixture afforded 49.2 g (88.5%) of the crude 2,3,3′,4′-biphenyltetracarboxylic acid. Recrystallization of the crude acid from water gave 2,3,3′,4′-biphenyltetracarboxylic acid (31.7 g), mp 193–204°. This acid was then refluxed with acetic anhydride (400 ml) for 3 hr. On cooling, 83 g (80%) of 2,3,3′,4′-BTDA was isolated: mp 195–205°; ir (KBr) 1840 (s, -COOCO-), 1770 cm^{-1} (s, -COOCO-).

Anal. Calcd for $C_{16}H_6O_6$: C, 65.31; H, 2.07. Found: C, 65.08; H, 2.07.

C.—A solution of 3,4,3′,4′-TMBT (18.6 g), concentrated hydrochloric acid (10 ml), and acetic acid (50 ml) in water (50 ml) was refluxed for 4 hr. On cooling with ice water, the crystals precipitated were filtered, washed with water, and dried to give 14.3 g (93%) of 3,4,3′,4′-biphenyltetracarboxylic acid, mp 295–305°. This acid (75 g) was then refluxed with acetic anhydride (250 ml) for 5 hr. On cooling, crystals precipitated and were filtered and dried to afford 52 g (78%) of BTDA: mp 295–308°; ir (KBr) 1820 (sh, -COOCO-), 1760 cm^{-1} (s, -COOCO-).

Anal. Calcd for $C_{16}H_6O_6$: C, 65.31; H, 2.07. Found: C, 65.45; H, 2.00.

Registry No.—Palladium, 7440-05-3; palladium acetate, 19807-27-3; toluene, 108-88-3; 2,2′-bitolyl, 605-39-0; 2,3′-bitolyl, 611-43-8; 2,4′-bitolyl, 611-61-0; 3,3′-bitolyl, 612-75-9; 3,4′-bitolyl, 73832-90-6; 4,4′-bitolyl, 613-33-2; *o*-xylene, 95-47-6; 2,3,2′,3′-tetramethylbiphenyl, 7495-46-7; 2,3,3′,4′-tetramethylbiphenyl, 5006-39-3; 3,4,3′,4′-tetramethylbiphenyl, 4920-95-0; dimethyl phthalate, 131-11-3; tetramethyl 2,3,3′,4′-biphenyltetracarboxylate, 36978-36-6; tetramethyl 3,4,3′,4′-biphenyltetracarboxylate, 36978-37-7; tetramethyl 2,3,2′,3′-biphenyltetracarboxylate, 36978-38-8; 3,4,3′,4′-biphenyltetracarboxylic acid, 22803-05-0; 2,3,3′,4′-biphenyltetracarboxylic acid, 36978-40-2; 2,3,3′,4′-biphenyltetracarboxylic acid dianhydride, 36978-41-3; 3,4,3′,4′-biphenyltetracarboxylic acid dianhydride, 2420-87-3.

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(12) Beilstein's Handbuch der Organischen Chemie," Vol. 9, 438 (1942).

(13) 3-Nitrophthalic acid was esterified with methanol and sulfuric acid, followed by hydrogenation with Raney Ni to dimethyl 3-aminophthalate, which was coupled by a modification of the reported procedure ("Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 222) to give 2,3,2′,3′-TMBT, mp 163–164° [167°, Beilstein's "Handbuch der Organischen Chemie," Vol. 9, 437 (1942)].