TABLE IV

RATES OF REACTION OF *vic*-DIOLS WITH LEAD TETRAACETATE IN 99% BENZENE–1% ACETIC ACID

Diol	k_{20} HOAc	k_{20} 99% C_6H_6–1% HOAc	$k_{C_6H_6\text{–HOAc}}/k_{\text{HOAc}}$
trans-I	0.03	30.0	1000
trans-II	0.06[a]	2.6[a]	43[a]
trans-Ia	282	151	0.54[b]
trans-Ib	689	348	.51
trans-Ic	369	339	.92
cis-Ic	...	80,300	...

[a] Criegee's data.[8] [b] Criegee obtained a ratio of 0.75.[8]

whose rates are retarded in solvent benzene, then important mechanistic conclusions can be derived from the data in Table IV. We have oxidized *trans*-I, *trans*-Ia, *trans*-Ib *and cis*- and *trans*-Ic diols with lead tetraacetate in the 99% benzene–1% acetic acid and found that all aryl substituted *trans*-diols showed a rate retardation. A rate increase was found for *trans*-I as with *trans*-II diols,[8] while a measurable rate was obtained for the first time for *cis*-Ic diol.[33] Thus the results strongly suggest mechanism 1 or 2 for *cis*- and *trans*-I and II diols as with most other diols,[1a,8] and some *alternative* mechanism, perhaps 3 or 4, for all the *trans*-1,2-diaryl-1,2-acenaphthenediols reported herein.

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(33) In this case, the concentration of acetic acid was probably too low to cause a measurable pinacol rearrangement.

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Dicarboxylation of Terphenyl

BY TOD W. CAMPBELL

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The Friedel–Crafts reaction of terphenyl with oxalyl chloride gives a high yield of 4,4''-dicarboxyterphenyl. A number of derivatives of this acid has been prepared, including a high molecular weight polyamide. The position of substitution has been shown unequivocally by conversion in four steps to the known 4,4''-dimethylterphenyl.

The synthesis of functionally substituted *p*-terphenyls is seldom straightforward and usually includes a coupling of aromatic systems, or formation of a ring by, for example, a Diels-Alder condensation. The field has been reviewed recently.[1] Direct substitution of *p*-terphenyl has yielded only a few derivatives. Thus, dinitration gives a mixture[2,3] while dibromination,[3–5] disulfonation[6] and diacylation[7,8] appear to take place in the 4- and 4''-positions. However, there is room for doubt regarding the position of substitution,[7,8] since reference compounds are lacking and the position of substitution has been assumed, not proved.

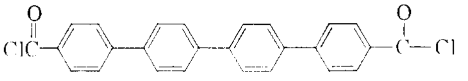
The carboxylation with oxalyl chloride[9] of terphenyl has now been investigated, and found to be a high-yield route to the previously unknown terphenyl-4,4''-dicarboxylic acid (I), the structure of which has been proved conclusively.

The dicarboxylation was carried out in carbon disulfide with excess oxalyl chloride and aluminum chloride in a yield of better than 90% of the acid after hydrolysis of the reaction mixture. The diacid formed pale yellow, high-melting leaflets. Interestingly, it was completely insoluble in aqueous potassium, sodium, lithium and ammonium hydroxides.

The diacid chloride II was readily prepared, as a pale yellow crystalline solid, soluble in many common solvents, easily hydrolyzed to the free diacid. It was readily converted to the dimethyl ester III. It was converted to a high molecular weight soluble polyamide (IV) by a low-temperature polymerization[10,11] with 2,5-dimethylpiperazine.

The structure of I and its derivatives was shown as follows. The acid chloride II was reduced with lithium aluminum hydride to the diol V, which was converted to the dihalide VI with thionyl chloride. Bis-(chloromethyl)-terphenyl was then hydrogenolyzed with lithium aluminum hydride to 4,4''-dimethylterphenyl (VII), identical to a sample prepared by an unequivocal route[12] (Fig. 1).

Attempts to dicarboxylate quaterphenyl and quinquephenyl[12] were not completely successful, although a small amount of crude quaterphenyldiacid chloride, probably the 4,4'''-derivative VIII,



VIII

was isolated. It was noteworthy for the very intense blue fluorescence of a dilute benzene solution even in diffuse sunlight.

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Experimental Part

Preparation of Terphenyldicarboxylic Acid.—A mixture of 45 g. of terphenyl, 150 g. of oxalyl chloride and 300 ml. of carbon disulfide was treated with stirring with 40 g. of anhydrous powdered aluminum chloride. The mixture immediately turned dark brownish-black. It was stirred in an ice-bath for one hour, then an additional 30 g. of anhydrous aluminum chloride was stirred in and the ice-bath removed. Stirring was continued overnight at room temperature, then the mixture was poured onto cracked ice to decompose the complex. The carbon disulfide was evaporated with a stream of nitrogen and the residual solid was filtered, washed repeatedly with dilute hydrochloric acid and dried. A pale yellow solid, 61.0 g., not melting at 400°, was obtained. A direct oxygen analysis of the crude dry reaction mixture showed 19.1% oxygen against a calculated value of 20.1 for terphenyldicarboxylic acid. A small portion of the diacid was recrystallized from dimethylacetamide in the form of yellow leaflets. These leaflets did not melt at 400° and contained 19.6% oxygen.

The dicarboxylic acid was completely insoluble in 10% aqueous lithium hydroxide, sodium hydroxide, potassium hydroxide and ammonia.

Preparation of Terphenyldicarbonyl Chloride.—For conversion to the diacid chloride, 61 g. of the crude dicarboxylic acid was refluxed with 450 g. of thionyl chloride and 20 ml. of pyridine. The solid dicarboxylic acid gradually went into solution and the reaction was assumed to be finished when the last traces of solid had dissolved. The excess thionyl chloride was removed by distillation. The crude diacid chloride was dissolved in boiling benzene, the solution filtered free from undissolved material, treated with a small amount of decolorizing carbon and filtered again. On cooling, the benzene deposited beautiful yellow leaflets, melting at 215°. The product, obtained in about 70% yield, sublimed very readily.

Anal. Calcd. for $C_{20}H_{12}O_2Cl_2$: C, 67.61; H, 3.41. Found: C, 67.59, 67.63; H, 3.34, 3.39.

The diacid chloride was readily converted to a dimethyl ester by boiling with a small amount of methyl alcohol. The solid dimethyl ester was recrystallized from dimethylformamide as well-formed, faintly yellow leaflets. These crystals showed a phase change at 305–306° on the Kofler hot-stage and a melting point of 315°.

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.2; H, 5.2; O, 18.6. Found: C, 75.8, 76.0; H, 5.6, 5.7; O, 18.35, 18.44.

The diacid chloride was boiled overnight with water. The solid was filtered, dried, and recrystallized from dimethylacetamide as pale yellow leaflets which did not melt below 400°.

Anal. Calcd. for $C_{20}H_{14}O_4$: C, 75.44; H, 4.43. Found: C, 75.21, 75.19; H, 4.34, 4.36.

Conversion of Terphenyldicarbonyl Chloride to Bis-(hydroxymethyl)-terphenyl—A solution of 4.7 g. of the diacid chloride in 250 ml. of hot tetrahydrofuran was added to a refluxing solution of 1 g. of lithium aluminum hydride in 250 ml. of tetrahydrofuran. An immediate exothermic reaction was noted and the mixture became somewhat gelatinous. Refluxing was continued overnight, then 50 ml. of isopropyl alcohol was added to decompose the excess hydride, followed by 500 ml. of water containing 25 ml. of concentrated hydrochloric acid. The milky mixture was heated on a steam-bath in a stream of nitrogen to remove excess tetrahydrofuran and the resulting suspension was centrifuged. The solid was separated, air-dried and recrystallized from dimethylformamide–water as very large, silvery leaflets. The yield of recrystallized product was 3.1 g. (81%). The product melted with decomposition at 325°.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.74; H, 6.25. Found: C, 83.0, 82.9; H, 6.4, 6.4.

Conversion of Bis-(hydroxymethyl)-terphenyl to Bis-(chloromethyl)-terphenyl.—One-half gram of bis-(hydroxymethyl)-terphenyl was mixed with 15 ml. of pyridine and 50 ml. of thionyl chloride and warmed over a heat lamp. Initially, the solid was insoluble. However, as time progressed, the solid gradually dissolved and the solution turned dark. After about 30 min. the mixture was poured into ice-water, and filtered. The light tan solid (0.7 g.) had a melting point of 250° on a hot bar. This crude product was dissolved in 100 ml. of boiling toluene, decolorized, and concentrated to about 60 ml. On cooling, leaflets of bis-(chloromethyl)-terphenyl crystallized. These melted at 254–256° dec.

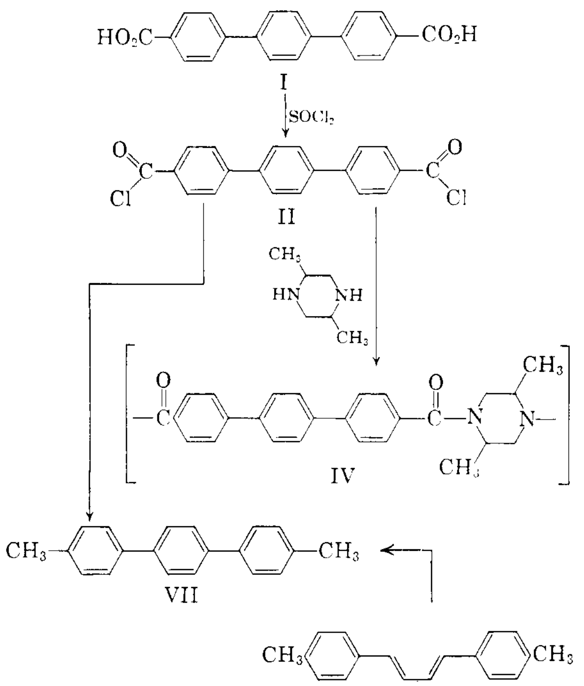

Fig. 1.—Terphenyldicarboxylic acid and derivatives.

Anal. Calcd. for $C_{20}H_{16}Cl_2$: Cl, 21.7. Found: Cl, 21.5.

Conversion of Bis-(chloromethyl)-terphenyl to 4,4''-Dimethylterphenyl.—To a solution of 0.25 g. of lithium aluminum hydride in 100 ml. of refluxing tetrahydrofuran was added 0.6 g. of bis-(chloromethyl)-terphenyl prepared as above. The mixture was refluxed overnight, cooled and decomposed by the addition of alcohol, and dilute hydrochloric acid. The product was filtered to give 0.46 g. of crude solid, m.p. 247–251°. This crude material was sublimed at 190° (0.5 mm.) to give 0.34 g. (71% yield) of 4,4''-dimethylterphenyl, m.p. 255–256°. The identity of the compound was substantiated by a mixed melting point with an authentic sample of 4,4''-dimethylterphenyl,[12] m.p. 255–56°.

Polyamide from the Diacid Chloride II and 2,5-Dimethylpiperazine.—A polyamide was prepared by reaction of aqueous 2,5-dimethylpiperazine with a chloroform solution of the diacid chloride according to techniques described in the literature.[10,11] The polymer had a high molecular weight, indicated by an inherent viscosity of 1.6 as measured at 30° on a 0.5% solution in a mixture of chloroform and formic acid (80:20). The polymer did not melt below 400° and could be cast to a clear, stiff, tough film from a mixture of chloroform and formic acid (80:20).

Carboxylation of Quaterphenyl.—Five grams of quaterphenyl was mixed with 30 ml. of oxalyl chloride, 75 ml. of carbon disulfide and 7 g. of aluminum chloride. This mixture was allowed to react at room temperature for 48 hours. It was then decomposed and the solid (7.1 g.) isolated, washed and dried. This solid was refluxed with pyridine (10 ml.) and thionyl chloride (100 ml.) for 24 hr. Excess thionyl chloride was evaporated, the residue was extracted into boiling xylene, and the solution was filtered, and cooled. A yield of 3.1 g. of dirty yellow leaflets was obtained. This product was dried and sublimed to a nearly colorless sublimate at 300° (0.15 mm.), yield 1.5 g. This product crystallized very well from toluene. The colorless leaflets melted partially at about 280°, but did not melt completely below 325°.

Anal. Calcd. for $C_{26}H_{16}O_2Cl_2$: C, 72.5; H, 3.7; O, 7.44. Found: C, 74.5, 75.1; H, 4.0, 4.1; O, 6.9.

A hot toluene solution fluoresced an intense blue, visible even in sunlight.

Carboxylation of Quinquephenyl.—Attempts to prepare quinquephenyldicarboxylic acid were unsuccessful. These experiments were run on 1-g. samples of quinquephenyl[12] using large excesses of oxalyl chloride and aluminum chloride in carbon disulfide solvent. After reaction over the weekend at room temperature, the reaction mixture was decomposed and worked up as in previous examples.

Anal. Calcd. for $C_{32}H_{22}O_4$: O, 13.6. Calcd for $C_{31}H_{22}O_2$: O, 7.5. Found: O, 8.5.

Sublimation of this product in a high vacuum at 300° separated a small amount of pale yellow product containing 0.6% oxygen. The residue now contained 9.4% oxygen. This would correspond to an average of about 1.2 carboxyls per quinquephenyl units.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Polyphosphoric Acid As a Reagent in Organic Chemistry. X. Two Yellow Hydrocarbons from Acetophenone

BY ROGER W. ROESKE, D. BRUCE BRIGHT, R. L. JOHNSON, W. J. DEJARLAIS, RICHARD W. BUSH AND H. R. SNYDER

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The action of polyphosphoric acid on acetophenone produces two crystalline yellow hydrocarbons (A and B) of the formula $C_{32}H_{24}$; other products isolated are benzoic acid, dypnone and a yellow substance (C) melting above 300°. The lower-melting yellow hydrocarbon (A) is isomerized to a colorless hydrocarbon (D). Studies of the reactions and spectra of A and D are made and structures are suggested for these hydrocarbons.

In an earlier paper of this series[1] it was shown that in the presence of polyphosphoric acid certain hindered aliphatic–aromatic ketones combine with reactive aromatic hydrocarbons to produce 1,1-diarylalkenes. For example, acetomesitylene and mesitylene give 1,1-dimesitylethylene. When acetophenone and benzene were treated with polyphosphoric acid the reaction took an entirely different course. The benzene functioned only as a solvent, and the acetophenone underwent self-condensation and hydrolysis. The five products isolated were benzoic acid, dypnone, two isomeric yellow hydrocarbons (A and B) of the molecular formula $C_{32}H_{24}$, and a high-melting yellow solid (C) which was so insoluble that no method for its purification was found.

The two yellow hydrocarbons, A and B, melted at 181 and 227°, respectively. The lower melting isomer (A) generated a beautiful deep green color in the presence of acids. For example, it dissolved in concentrated sulfuric acid to give a solution so deeply colored as to appear black, but on dilution with water the yellow hydrocarbon A was regenerated. It could be extracted from benzene solution with concentrated sulfuric acid, and in this way could be separated from the higher-melting isomer (B), which remained in the benzene.

The conditions found to be most satisfactory for the preparation of the yellow hydrocarbon A involved a reflux period of seven hours. The hydrocarbon was produced in 14.5% yield in a relatively pure state. The amount of dypnone isolated from the reaction mixture was dependent on the reaction time. With a reflux period of one hour, dypnone was obtained in 34% yield, 58% conversion, and the yields decreased with longer reflux periods. The possibility that dypnone is an intermediate in the formation of A and B was tested by treating a benzene solution of dypnone with polyphosphoric acid. In addition to small amounts of compound C and benzoic acid, A was isolated from the reaction. The crude yellow product, however, had a wide melting point range, and some of the material melted at 175–205°. Presumably a mixture of A and B was formed. Similar results were obtained when a mixture of acetophenone and dypnone in a 2 to 1 molar ratio was used. Thus, it appears likely that dypnone is an intermediate in the formation of both A and B as well as C, but the possibility remains that any of the products was formed from acetophenone liberated by the hydrolysis of the dypnone used in these experiments. In an effort to obtain a substituted compound related to A or B, *p*-bromoacetophenone was treated with polyphosphoric acid, but the only material isolated was 4,4′-dibromodypnone. The yield was 35%.

The yellow hydrocarbon A exhibits a high degree of reactivity in comparison to the diarylalkenes[1] which were obtained from similar reactions. The substance decolorizes bromine and potassium permanganate solutions and turns green-black in the presence of strong acids. The oxidation of A with dilute nitric acid gave benzoic and *p*-nitrobenzoic acid. When chromic anhydride in acetic acid was employed as the oxidizing agent, a neutral yellow material that melted with decomposition was obtained. However, the product could not be purified by recrystallization or chromatography.

A tetrahydro derivative of A was obtained by employing a Raney nickel catalyst and hydrogen at 1400 p.s.i. and 100°. It was found that the treatment of A with lithium aluminum hydride caused the immediate formation of a dark green color. After hydrolysis of the reaction mixture a colorless substance was isolated, the analysis of which corresponded to a dihydro derivative. The same dihydro derivative was obtained by reduction with hydriodic acid in refluxing acetic acid solution. A colorless hexahydro derivative was obtained by reduction of A with a solution of sodium in liquid ammonia. When A was treated with butyllithium and carbonated, an acid having the empirical formula $C_{37}H_{34}O_2$ was formed. The

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[1] H. R. Snyder and R. W. Roeske, THIS JOURNAL, **74**, 5820 (1952).