TABLE I

ORGANO PLATINUM COMPOUNDS: ANALYSES, CHEMICAL, PHYSICAL AND OPTICAL PROPERTIES

		Optical data[a]			Solubilities[b]									Platinum, %		
Platinous chlorides	Color	Form	Bire.	Ext. angle	$CHCl_3$	Ether	Bz	EtOH	Glac. HAc	Acetone	Water	NaCl soln.	M.p., °C.	Calcd.	Found	
Cyclohexene	sl. or.	l. silky needles[c]	...	par. sym. obl.	s.	s.	sl. s.	v. s.	ins.	v. s.	...	ins.	145–146	56.07	56.0	56.0[i]
Dipentene	f. yel.	biax. pr.[c]	low	34°	v. s.	ins.	v. sl.	ins.	ins.	s.	...	ins.	151–152	48.53	48.4[d]	48.3[e,i]
Pinene	f. yel.	prisms[c]	high	6°	v. s.	sl.	s.	sl.	sl.	s.	...	ins.	138–141	48.53	48.6	48.6
Ethylene	or.	tablets[c]	high	32°	s.	v. s.	s.	v. s.	ins.	v. s.	sl.[g]	sl.	170–180[f]	66.35	65.7	65.7
Isobutylene	or.	rhb. pl.	...	18°	v. s.	v. s.	v. s.	v. s.	sl.	v. s.	ins.[g]	v. s.	144–145	60.59	60.6	60.7
Styrene	or.	hex. pr.[c]	fair	30°	s.	s.	sl.	...	v. sl.	s.	ins.	v. sl.	169–171	52.73	52.6	52.6
Stilbene	or.	sm. hex. pr.[c]	high	30°	v. s.[h]	s.	v. sl.	v. sl.	ins.	v. s.	...	ins.	191–192	43.75	43.7	43.7[k]
trans-Dichloroethylene	or.	cryst.[c]	high	par.	s.[h]	...	s.	...	...	s.	...	...	155–160	53.77	54.6	54.7
Cyclohexene $\cdot PtBr_2$	or.	l. sl. need.[c]	fair	par.	s.	ins.	v. sl.	v. sl.	ins.	sl.	...	...	150–151	44.66	44.5	44.7
Styrene $\cdot PtBr_2$	rose	hex. pr.[c]	fair	32°	s.	ins.	sl.	ins.	ins.	sl.	...	ins.	153–154	42.52	42.4	42.5

[a] Abbreviations: par., parallel; sym., symmetrical; obl., oblique; ext., extinction; bire., birefringence; or., orange; yel., yellow; f., faint; l., long; sm., small; pl., plates; sl., slender; pr., prisms; hex., hexagonal. [b] Abbreviations: s., soluble; v., very; sl., slightly soluble; ins., insoluble. [c] Anisotropic. [d] Prepared from platinous chloride and dipentene. [e] Prepared from platinic chloride and dipentene. [f] After standing in air for about three weeks it decomposes at 125–130°. [g] Also in petroleum ether. [h] Also in nitrobenzene. [i] % Chlorine calcd.: 20.37. Found: 20.34 and 20.44. [j] % Chlorine calcd.: 17.63. Found: 17.7 and 17.7. [k] % Chlorine calcd.: 15.89. Found: 15.8 and 15.8.

The compound decomposes at 168–170°.

Solubility.—This compound is soluble in acetone, chloroform and ether; and slightly soluble in glacial acetic acid, alcohol and benzene.

Summary

1. It has been shown that anhydrous platinic halides react with ethylenic substances to give coördination compounds of the type $(Un \cdot PtX_2)_2$.

2. The behavior of these coördination compounds with various reagents has been described.

3. A ring formula has been proposed for the coördination compounds.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Orientation of *p*-Methoxydiphenyl in the Friedel and Crafts Reaction

BY L. F. FIESER AND CHARLES K. BRADSHER

In the course of certain synthetic work the occasion arose to investigate the condensation of *p*-methoxydiphenyl with succinic anhydride in the presence of aluminum chloride, and it was found that the reaction proceeds smoothly in nitrobenzene solution, giving a mixture of two isomers. As the higher melting keto acid forms a sparingly soluble sodium salt by means of which it can be removed from the mixture, a separation is easily accomplished. It was found that about two-thirds of the substitution occurs in the para position of the unsubstituted ring (I) and the remainder ortho to the methoxyl group (II). In establishing the structures the keto acids were first oxidized, best with permanganate in the case of I and with hypobromite for II, to the methoxydiphenyl carboxylic acids III and IV. The hydroxy acids obtained on demethylation corresponded in melting point to substances described in the patent literature, 4-hydroxy-4′-carboxydiphenyl having been obtained through the nitro derivative of the 4-carboxylic acid[1] and 3-carboxy-4-hydroxydiphenyl from the 4-hydroxy compound through the aldehyde[2] and by the Kolbe reaction.[3] In order to establish the structures completely exhaustive oxidations were conducted on the phenol III and the keto acid II. These yielded terephthalic acid and benzoic acid, respectively, in accordance with the formulation.

It was of interest to see whether the solvent in the Friedel and Crafts reaction plays any part in determining the ratio of homo- and hetero-nuclear substitution products, and as the condensation of *p*-methoxydiphenyl with succinic anhy-

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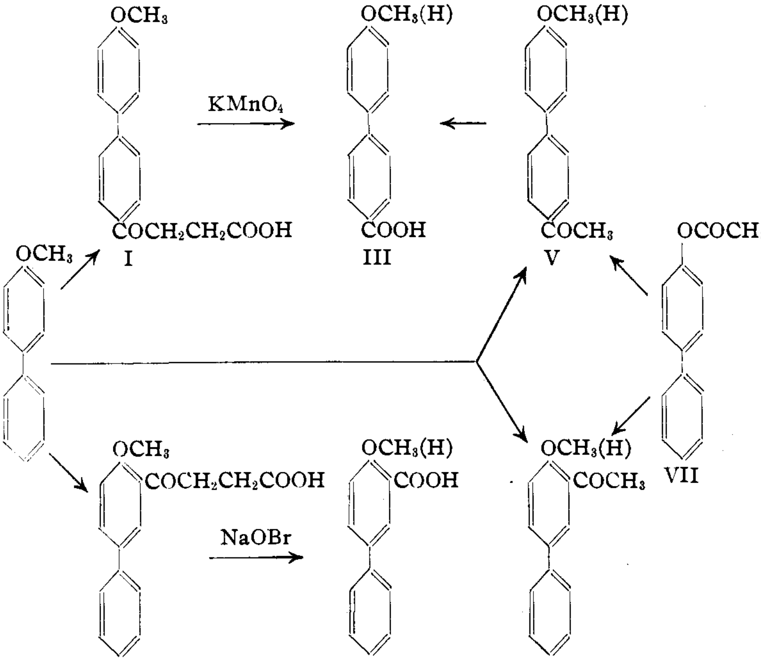
(1) French Patent 735,846; English Patent 390,556.

(2) American Patent 1,839,526.

(3) American Patent 1,941,207.

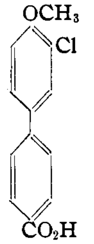


I III V VII II IV VI

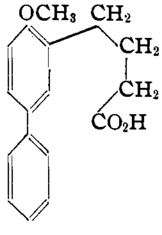
dride did not proceed satisfactorily in solvents other than nitrobenzene the reaction with acetyl chloride was investigated for this purpose. Two isomers were invariably obtained and there was no appreciable difference in the results using nitrobenzene, tetrachloroethane or carbon bisulfide. The isomer formed in larger amounts and having the higher melting point was found to be 4′-aceto-4-methoxydiphenyl (V) for it yielded III (ether) on oxidation with permanganate. In analogy with the above results the second product, isolated from the mother liquor as the semicarbazone, is very probably VI. With the two aceto compounds available it was of interest to investigate the Fries rearrangement of the acetate of *p*-hydroxydiphenyl (VII), for although Blicke and Weinkauff[4] studied the rearrangement of the benzoate they did not establish rigorously the structure of the sole reaction product isolated. In the present case it was found that the acetyl group migrates to both the *o*- and the *p*′-positions.

In general *p*-methoxydiphenyl resembles β-methoxynaphthalene in giving rise to Friedel and Crafts substitutions both ortho to the methoxyl group and at the most remote position of the second nucleus.

An additional observation worthy of note is that on oxidizing β-(4-methoxy-4′-xenoyl)-propionic acid (I) with sodium hypochlorite the product, separated from excess reagent as the sodium salt, was found to contain chlorine. The structure VIII was established by the preparation of the acid from the known[5] 3-chloro-4-methoxydiphenyl by condensation with acetyl chloride and permanganate oxidation. In this Friedel and Crafts reaction the unsubstituted ring alone appears to be attacked. The corresponding 3-bromo compounds also were prepared. Another interesting observation is that all attempts to cyclize the butyric acid derivative IX with sulfuric acid or through the acid chloride were unsuccessful. The ester of IX was also converted into the oxalyl derivative and submitted to the Bougault reaction with sulfuric acid, but a ring closure was not achieved. This evidently constitutes an additional case of the inhibitory influence on cyclizations often exerted by a *m*-methoxyl group.[6]



VIII



IX

Experimental Part

Condensation of *p*-Methoxydiphenyl with Succinic Anhydride.—A solution of 50 g. of the ether and 29.9 g. of succinic anhydride in 500 cc. of nitrobenzene was cooled in an ice-bath and 67.5 g. of aluminum chloride was added in small portions with stirring. The mixture was stirred cold for six hours and at room temperature for an equal period and then treated with ice and acid and the solvent removed with steam. The solid residue was dissolved in 1.5 liters of water containing 40 g. of sodium carbonate and after clarifying the hot solution with Norite and cooling to 0° the sodium salt of **β-(4-methoxy-4′-xenoyl)-propionic acid** (I) separated as a curdy precipitate. The collected salt was suspended in hot water and acidified, giving a light gray precipitate of the free acid, m. p. 192–195°, yield 18.9 g. (24.5%). Crystallized from acetic acid in which it

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[4] Blicke and Weinkauff, THIS JOURNAL, **54**, 330 (1932).

[5] Colbert, Meigs and Mackin, *ibid.*, **56**, 202 (1934).

[6] Compare Graves and Adams, *ibid.*, **45**, 2439 (1923); Gardner and Adams, *ibid.*, **45**, 2455 (1923); Jacobson and Adams, *ibid.*, **46**, 1312 (1924).

is moderately soluble, the acid forms colorless plates or needles melting at 200–201° with slight darkening in contact with the glass.

The mother liquor remaining after removal of the salt was treated at the boiling point with sodium chloride until nearly saturated, and on cooling the sodium salt of **β-(4-methoxy-3-xenoyl)-propionic acid** (II) separated in a crystalline condition. The free acid precipitated from a clarified solution was nearly pure, m. p. 147–148°, yield 46.5 g. (60%). It is much more soluble than the isomer and forms small needles from ether and a microcrystalline powder from alcohol, m. p. (camphor-like) 155°, clear.

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.81; H, 5.67. Found: (I) C, 72.02; H, 5.63; (II) C, 72.05; H, 5.90.

The methyl ester of I, microcrystals from dilute acetic acid, has a camphor-like melting point, liquefaction beginning at 99° and the crystal skeleton disappearing at 110°. **The methyl ester** of II forms small plates from ether–pe-petroleum ether, m. p. 48–49°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.09. Found: (I-ester) C, 72.31; H, 5.93; (II-ester) C, 72.12; H, 6.06.

Clemmensen Reduction.—The keto acids I and II were reduced in the form of the methyl esters (crude) by the ordinary Clemmensen procedure and the resulting acids were conveniently purified by salting out the sodium salts from the alkaline solutions. **γ-(4-Methoxy-4′-xenyl)-butyric acid**, obtained in a small-scale experiment in 20% yield, formed microcrystals from dilute alcohol, m. p. 148–149° with previous softening. **γ-(4-Methoxy-3-xenyl)-butyric acid** (IX) formed long, colorless needles from dilute alcohol, m. p. (camphor-like) 109°; yield 54–58%.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.56; H, 6.72. Found: (4′-isomer) C, 75.62; H, 6.64; (3-isomer) C, 75.69; H, 6.49.

The acid IX was either sulfonated or unattacked in attempted cyclizations with sulfuric acid of various strengths, and the acid chloride seemed either not to react or to yield polymeric products when treated with condensing agents. Polymerization seemed to occur also in the Bougault condensation of the oxalyl derivative of the ethyl ester, prepared and treated in the usual way.[7]

Oxidation to Methoxydiphenyl Carboxylic Acids.—The keto acid I (2.5 g.) was best oxidized in a solution of potassium hydroxide (2.5 g.) and water (200 cc.) with potassium permanganate (6.6 g.) at the temperature of the steam-bath. The precipitated dioxide was dissolved, after cooling, with sulfur dioxide and the solution was acidified and heated to coagulate the **4-methoxy-4′-carboxydiphenyl** (III) which separated; yield 1.5 g. This formed a microcrystalline powder from glacial acetic acid, m. p. 248–249°.

For the preparation of **3-carboxy-4-methoxydiphenyl** (IV) a solution of 5 g. of the keto acid II and 14 g. of sodium hydroxide in 200 cc. of water was treated at 10° with 14 g. of bromine. After twelve hours the solution was treated with sulfur dioxide, followed by hydrochloric acid. The precipitated acid was coagulated by digestion at the boiling point; yield 3 g. (75%). Distilled in vacuum and crystallized from ether the acid formed slightly yellow plates, m. p. 166–167°.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.65; H, 5.31. Found: (III) C, 73.49; H, 5.66; (IV) C, 73.30; H, 5.59.

The methyl ester of III forms plates from methyl alcohol, m. p. 172–173°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.35; H, 5.82. Found: C, 74.31; H, 6.15.

Demethylation.—The methoxy acids III and IV were refluxed with glacial acetic acid (20 cc. for a 3-g. lot) and 48% hydrobromic acid (6 cc.) for four hours and the solutions were concentrated and diluted to crystallization. **4-Hydroxy-4′-carboxydiphenyl** was crystallized from dioxane–cyclohexane, forming transparent (solvated) needles, m. p. (dry) 293–294°. **3-Carboxy-4-hydroxydiphenyl** formed needles from ether–cyclohexane, m. p. 212–213°.

Anal. Calcd. for $C_{13}H_{10}O_3$: C, 72.86; H, 4.71. Found: (4′-acid) C, 72.62; H, 5.05; (3-acid) C, 72.73; H, 5.08.

The 4′-methyl ester formed plates from alcohol, m. p. 224–225°; the **3-ester** crystallized from petroleum ether as prismatic needles, m. p. 93–94°.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 73.65; H, 5.31. Found: (4′-ester) C, 73.97; H, 5.64; (3-ester) C, 73.67; H, 5.42.

Exhaustive Oxidation.—A hot solution of 0.9 g. of 4-hydroxy-4′-carboxydiphenyl and 3 g. of potassium hydroxide in 100 cc. of water was treated in the course of two hours with a solution of 5.75 g. of permanganate. The crude oxidation product was esterified and the ester (0.3 g.) distilled in vacuum and crystallized from methyl alcohol, giving flat needles of dimethyl terephthalate, m. p. 140–141°.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.82; H, 5.19. Found: C, 61.66; H, 5.52.

β-(4-Methoxy-3-xenoyl)-propionic acid on oxidation with excess alkaline permanganate gave benzoic acid, which was extracted with ether from the residue after evaporation, sublimed, and fully identified.

3-Chloro-4-methoxy-4′-carboxydiphenyl (VIII).—(a) β-(4-Methoxy-4′-xenoyl)-propionic acid (5 g.) was heated with 720 cc. of 2.5% sodium hypochlorite solution for several hours on the steam-bath and on nearly saturating the solution with sodium chloride and cooling, the sodium salt of the chlorinated acid separated. It was collected and washed with salt solution, and the free acid was liberated and crystallized from dilute acetic acid; small needles, m. p. 275–276°.

Anal. Calcd. for $C_{14}H_{11}O_3Cl$: C, 63.98; H, 4.23. Found: C, 63.96; H, 4.62.

The methyl ester formed cottony needles from methyl alcohol, m. p. 145–146°.

Anal. Calcd. for $C_{15}H_{13}O_3Cl$: C, 65.08; H, 4.74. Found: C, 65.30; H, 4.82.

(b) 3-Chloro-4-methoxydiphenyl (5 g.) was first converted with acetyl chloride (2 g.) and aluminum chloride (3.4 g.) in carbon bisulfide medium into **3-chloro-4-methoxy-4′-acetodiphenyl,** which was vacuum distilled and crystallized from alcohol; needles, m. p. 109–110°.

Anal. Calcd. for $C_{15}H_{13}O_2Cl$: C, 69.07; H, 5.03. Found: C, 69.17; H, 5.30.

The ketone (1 g.) was oxidized with potassium permanganate (1.21 g.) in a hot, stirred, alkaline medium, and the purified product (0.35 g.) and its methyl ester were com-

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(7) Fieser and Hershberg, THIS JOURNAL, 57, 1851 (1935).

pared with the above samples and found to give no depressions in the melting points.

Bromo Compounds.—Using analogous methods the following compounds were prepared: **3-bromo-4-methoxy-4′-acetodiphenyl** (a), plates from methyl alcohol, m. p. 97–98°; **3-bromo-4-methoxy-4′-carboxydiphenyl** (b), needles from tetrachloroethane, m. p. 270–271°; methyl ester (c), long needles from alcohol, m. p. 148–149°.

Anal. Calcd. (a) C, 59.02; H, 4.30; (b) C, 54.72; H, 3.62; (c) C, 56.07; H, 4.08. Found: (a) C, 59.10; H, 4.63; (b) C, 54.66; H, 3.89; (c) C, 55.91; H, 3.95.

Condensation of *p*-Methoxydiphenyl with Acetyl Chloride.—The reaction of the ether (5 g.) and acetyl chloride (2.2 g.) in the presence of aluminum chloride (4 g.) was run in boiling carbon bisulfide, in tetrachloroethane at 0–20°, and in nitrobenzene at 0–20°. There was little difference in the total yield or the ratio of isomers in the three cases, although tetrachloroethane seemed to give slightly better results (65% yield) than the other solvents. A separation is easily accomplished with ether, which readily dissolves the low-melting isomer (VI) and leaves the other ketone (V) as a residue, and in each case the high-melting compound was found to comprise 65–75% of the total. This substance, **4-methoxy-4′-acetodiphenyl** (V), forms microcrystals from methyl alcohol, m. p. 153–154°. On oxidation with alkaline permanganate it gave an acid identical with III. **3-Aceto-4-methoxydiphenyl** (VI) was found in the ether mother liquor contaminated with unchanged *p*-methoxydiphenyl. It was easily separated from this substance and purified through the semicarbazone, which gives plates from alcohol. On hydrolysis with boiling 2 *N* hydrochloric acid the ketone was obtained and crystallized from dilute methyl alcohol; plates, m. p. 62–63°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.61; H, 6.24. Found: (V) C, 79.65; H, 6.34; (VI) C, 79.66; H, 6.43.

Fries Rearrangement.—4-Acetoxydiphenyl (5 g.) was intimately mixed with aluminum chloride (3.5 g.) and carbon disulfide (20 cc.) and heated to evaporate the solvent. The residue was heated in a bath at 140° for thirty minutes and then decomposed with dilute hydrochloric acid and extracted with ether. The rearranged material was extracted from the washed solution with dilute alkali and recovered as a solid by acidification. **4-Hydroxy-4′-acetodiphenyl**, the less soluble isomer, was obtained by crystallization of the crude material to constant melting point from benzene; small needles, m. p. 206–207° (0.2 g.). It gave on methylation a product identical with the ether V described above. The material recovered from the benzene mother liquor was taken up in alcohol (50 cc.) and treated with an aqueous solution of semicarbazide hydrochloride (1.1 g.) and sodium acetate (0.8 g.). On standing yellow crystals of a semicarbazone separated (0.95 g.; m. p. >270°) and this was hydrolyzed with boiling 2 *N* hydrochloric acid. After crystallizing the recovered ketone from petroleum ether **3-aceto-4-hydroxydiphenyl** was obtained as small prisms, m. p. 61–62°, and on methylation it formed an ether, m. p. 62–63°, which did not depress the melting point of 3-aceto-4-methoxydiphenyl.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.21; H, 5.71. Found: (4′-isomer) C, 79.37; H, 6.01; (3-isomer) C, 79.19; H, 5.83.

Summary

In the Friedel and Crafts reaction with succinic anhydride and with acetyl chloride 4-methoxydiphenyl is substituted in both the 3- and the 4′-positions and solvents have little influence on the ratio of the isomers produced. The Fries rearrangement of 4-acetoxydiphenyl also proceeds in these two directions.

The closing of a six-membered ring at the 2-position of diphenyl is inhibited by a *m*-methoxyl group at position 4.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.

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[CONTRIBUTION FROM RÖHM AND HAAS COMPANY, INC.]

The Condensation of Phenols with Ethanolamine and Formaldehyde

BY HERMAN ALEXANDER BRUSON

It has been known for some time that amines catalyze the condensation between phenols and formaldehyde to form resins. The mechanism of this reaction is still obscure.

When phenols are condensed with molecular equivalents each of formaldehyde and secondary amines, such as dimethylamine or piperidine, tertiary amines are formed.[1]

Décombe has shown that the products thus obtained are, without doubt, *o*-hydroxybenzylamino derivatives.[2]

Morpholine is particularly prone to form well-defined, crystalline hydroxybenzylmorpholines with a variety of monohydric or polyhydric phenols and formaldehyde.[3]

In a study of this reaction with other amines, it has now been found that *β*-aminoethanol can be combined with formaldehyde and phenols to yield hydroxybenzylaminoethanols. The condensation is, however, complicated by the formation of resinous materials which in some cases form the main product. It has been found possible, by intro-

(1) Bayer, German Patent 89,979, 92,309 (1895).

(2) J. Décombe, *Compt. rend.*, **196**, 866 (1933); **197**, 258 (1933).

(3) H. Bruson, U. S. Patent 2,040,039, 2,040,040 (1936).