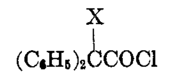
TABLE I
REACTIONS OF PHOSPHORUS PENTACHLORIDE

Starting material	Mol of PCl_5 per mol of starting material	Conditions, °C, (hr)	Purification	Product	Yield, %	Mp or bp, °C (mm)	Lit. mp or bp, °C
Toluene	0.5	Reflux, 110 (40)	Distillation	Benzyl chloride[a]	97[b]	68–70 (12)	179[c]
Toluene	2	Sealed tube 140–150 (18)	Distillation	Benzylidene chloride[a]	38	105–107 (12)	214[c]
Diphenylmethane	1	140–150 (18)	Distillation	Benzhydryl chloride[a]	78	160–162 (12)	161–162[d]
Diphenylmethane	3	140–150 (18)	Distillation	Diphenylmethylene chloride[a]	90	170–173 (12)	172[e]
Triphenylmethane	2	140–150 (18)	Recrystallization, benzene–hexane[f]	Triphenylmethyl chloride[a]	93	111–113	113–114[f]
Diphenylacetyl chloride[h]	2	140–150 (18)	Recrystallization, pentane	Diphenylchloroacetyl chloride[i]	85	49–51	50[j]
1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p'*-DDT)	2	Sealed tube 180–200 (18)	Recrystallization, ethanol	1,1,1,2-Tetrachloro-2,2-bis(*p*-chlorophenyl)ethane[g]	88	90–92	90–91[g]

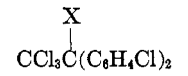
[a] The infrared spectrum was identical with that of the authentic material. [b] This yield was based on unrecovered toluene. Based on phosphorus pentachloride, it was 42%. [c] N. H. Lange, "Handbook of Chemistry," 7th ed, Handbook Publishers, Inc., Sandusky, Ohio, 1949. [d] H. Gilman and J. E. Kirby, *J. Amer. Chem. Soc.*, **48,** 1735 (1926). [e] L. Gattermann and H. Schulze, *Ber.*, **29,** 2944 (1896). [f] L. Gattermann and H. Wieland, "Die Praxis des organischen Chemikers," 39th ed, Walter de Gruyther & Co., Berlin, 1959, p 298. [g] The melting point of this material was not depressed by mixture with the authentic material. [h] H. Staudinger, *Ber.*, **44,** 1619 (1911). [i] The identity of this material was established by conversion into ethyl diphenylchloroacetate, mp 42–44° (lit.[9] mp 43–44°), by solution in ethanol, and by conversion into mandelic acid, mp and mmp 117–118°, by reflux in potassium carbonate solution. [j] H. Bickel, *Ber.*, **22,** 1539 (1889).

Diphenylacetyl chloride, IX, heated with excess phosphorus pentachloride gave diphenylchloroacetyl chloride, X, in 85% yield.



$(C_6H_5)_2\overset{X}{\overset{|}{C}}COCl$

IX, X = H
X, X = Cl



$CCl_3\overset{X}{\overset{|}{C}}(C_6H_4Cl)_2$

XI, X = H
XII, X = Cl

When 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, the insecticide *p,p'*-DDT, XI, was heated with phosphorus pentachloride at 180–200° for 18 hr, an 88% yield of 1,1,1,2-tetrachloro-2,2-bis(*p*-chlorophenyl)ethane, XII, was obtained. The preparation of XII is usually from XI in two steps, the dehydrochlorination of XI with base to give 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene, XIII, followed by the addition of chlorine to the ethylenic double bond of XIII to give XII.[9]

$$Cl_2C{=}C(C_6H_4Cl)_2$$

XIII

To test the possibility that XIII might be an intermediate in our conversion of XI to XII with phosphorus pentachloride, XIII was heated with phosphorus pentachloride. An almost quantitative yield of XII was obtained. Hence all that can be said is that XIII may be an intermediate in this reaction. The use of phosphorus pentachloride for the addition of chlorine to an ethylenic double bond is known.[10] The chlorination of the other compounds in Table I cannot involve such an olefinic intermediate.

The several compounds mentioned above in which benzylic hydrogen is replaced by chlorine on heating with phosphorus pentachloride suggest that this is a general reaction.

Experimental Section

Replacement of Benzylic Hydrogen with Chlorine Using Phosphorus Pentachloride.—A reaction typical of those outlined in Table I is described for the preparation of XII. A mixture of 5.0 g (0.013 mol) of XI and 7.2 g (0.026 mol) of phosphorus pentachloride was sealed in a 40-ml glass tube and heated at 180–200° for 18 hr. The cooled reaction mixture was added to ice water and stirred until the excess phosphorus pentachloride and the phosphorus trichloride were decomposed. The insoluble material was taken up in ether and the ether layer was dried with magnesium sulfate and evaporated. The residue was recrystallized from ethanol: yield 4.5 g (88%); mp 90–92° (lit.[9] mp 91–92°).

Registry No.—Phosphorus pentachloride, 10026-13-8; toluene, 108-88-3; diphenylmethane, 101-81-5; triphenylmethane, 519-73-3; IX, 1871-76-7; XI, 50-29-3.

(9) O. Grummitt, A. Buck, and A. Jenkins, *J. Amer. Chem. Soc.*, **67,** 155 (1945).

(10) L. Spiegler and J. M. Tinker, *ibid.*, **61,** 940 (1939).

The Platinum-Catalyzed Air Oxidation of Hindered Phenols

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Although the platinum-catalyzed air oxidation of aliphatic alcohols has been widely studied, only minor attention has been devoted to hydroxy aromatics.[1]

(1) K. Heyns and H. Paulsen in "Newer Methods of Preparative Organic Chemistry," Vol. 2, W. Foerst, Ed., F. K. Kirchner, translator, Academic Press, New York and London, 1963, p 303.

TABLE I

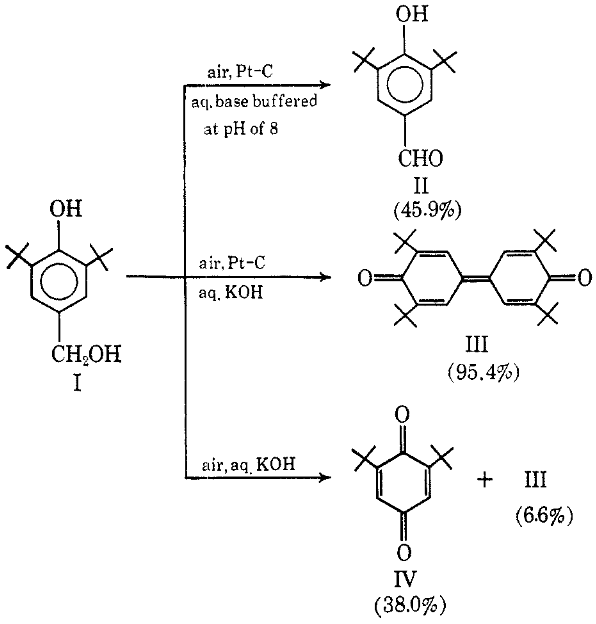
PHENOL OXIDATIONS

Phenol (0.05 mol)	Solution	Catalyst, g	Temp, °C	Time, hr	Product, % yield
I	H_2O, 100 cc KOH, 0.055 *M*	None	58	5.5	Diphenoquinone (III), 6.6 Benzoquinone (IV), 38.0
I	H_2O, 100 cc KOH, 0.055 *M*	10% Pt-C, 0.98	59	2.5	Diphenoquinone (III), 95.4[a]
I	H_2O, 50 cc[b] KH_2PO_4, 0.34 g 0.11 *N* NaOH, 39 cc	10% Pt-C, 0.98	62	18.0	Aldehyde (II), 45.9
I	H_2O, 100 cc	10% Pt-C, 0.98	63	13.0	Aldehyde (II), 15.9
I	Benzene, 60 cc	PtO_2,[c] 1.14	62	15.5	Aldehyde (II), 14.9 Red, viscous syrup
2,6-Di-*t*-butylphenol	Benzene, 60 cc	PtO_2,[c] 1.0	60	3.0	Diphenoquinone (III), 96.2[a]

[a] Before recrystallization. [b] A buffered solution of pH 8. I. M. Kolthoff and H. A. Lastinen, "pH and Electrotitrations," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1941, p 35. [c] Activated by hydrogenation.

It was the purpose of this work to examine an aromatic system containing both alcoholic and phenolic groups to see if one could be preferentially oxidized in the presence of the other over a platinum catalyst. Indeed, it was found that 3,5-di-*t*-butyl-5-hydroxybenzyl alcohol (I) could be oxidized to either the corresponding aldehyde (II) or to quinoid products, depending upon reaction conditions (Scheme I). This is believed to be the first application of platinum catalysis in phenol oxidation.

SCHEME I



In aqueous solution, buffered at a pH of 8, 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (II) was obtained in 45.9% yield. Unreacted alcohol (I) was also recovered, giving an overall material balance of 92% and showing that little or no side reaction occurred. Similar oxidation under slightly acidic conditions (pH 5–6) also produced the aldehyde (II), but in low yield.

In strong aqueous base, air oxidation of I over Pt-C gave a nearly quantitative yield of 3,3′,5,5′-tetra-*t*-butyldiphenoquinone (III). In the absence of platinum 6.6% of the diphenoquinone (III) and 38.0% of the benzoquinone (IV) were obtained.

The air oxidation of I over Pt in benzene gave a red, viscous syrup (which may contain some diphenoquinone) and a 14.9% yield of the aldehyde (IV). Under essentially identical conditions, the oxidation of 2,6-di-*t*-butylphenol afforded the diphenoquinone (III) in excellent yield.

The mechanism of the oxidative coupling of phenols has received considerable attention and is generally believed to proceed through the coupling of the intermediate dienone radicals.[2] The results obtained here for I can be rationalized by assuming that the phenoxide ions, formed in the very basic solutions, are rapidly oxidized by platinum to dienone radicals which couple, giving the observed diphenoquinone (III). Under neutral or slightly acidic conditions, phenoxide ions are not present and typical platinum-catalyzed oxidative dehydrogenation[1] of the alcoholic group is obtained. When I is air oxidized in strong base but in the absence of platinum, dienone radicals are formed at a much slower rate, permitting O_2 oxidation to the benzoquinone (IV).[3]

Rationalization of the oxidation of 2,6-di-*t*-butylphenol, which gave coupled product in neutral solution, is less clear and may proceed through an oxidative dehydrogenation on the surface of the platinum catalyst.

Experimental Section

Oxidation and Identification of Products.—The oxidations were carried out by placing the phenol, catalyst,[4] and solvent in a 300-ml rocking autoclave which was then pressured with about 400–500 psi of air (see Table I).

When water was the solvent, both catalyst and quinone products were collected by filtration, after which the product was taken up in benzene and the insoluble catalyst removed by filtration. The products were recovered by evaporation of the benzene solution to dryness. When benzene was the solvent, the catalyst was simply removed by filtration and the benzene solution evaporated to dryness to recover the oxidation products. When water was the solvent and no catalyst was used, the product was obtained by filtration.

Diphenoquinone and benzoquinone were separated by fractional crystallization from absolute ethanol. When 3,5-di-*t*-butyl-4-hydroxybenzaldehyde was the product, it was separated from catalyst and starting material by extraction with hot ethanol. The catalyst was removed by filtration and the aldehyde obtained by crystallization.

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(2) G. Scott, "Atmospheric Oxidation and Antioxidants," Elsevier Publishing Co., Amsterdam, London, and New York, 1965, Chapter 4, p 115.

(3) It should be noted that the oxidations were carried out in a rocking autoclave where oxygen diffusion into solution is very slow.

(4) PtO_2 was activated by hydrogenation at about 225 psi and at room temperature until hydrogen uptake was complete. Pt-C required no activation.

3,3′,5,5′-Tetra-*t*-butyl-4,4′-diphenoquinone was purified by recrystallization from absolute ethanol; it melted at 242–243° (lit.[5] 246°).

Anal. Calcd for $C_{28}H_{40}O_2$: C, 82.30; H, 9.87. Found: C, 82.3; H, 9.9.

The infrared spectrum was identical with that of the authentic compound[6] and the nmr showed nine *t*-butyl hydrogens for each vinyl hydrogen.

2,6-Di-*t*-butyl-1,4-benzoquinone was purified by recrystallization from absolute ethanol and melted at 66–67° (lit.[7] 67.5–68.5°). Its infrared spectrum matched that of the authentic compound in Sadtler and its nmr showed a 9:1 ratio of *t*-butyl to vinyl hydrogens.

3,5-Di-*t*-butyl-4-hydroxybenzaldehyde was recrystallized from absolute ethanol and melted at 187–188° (lit.[8] 189°). Its 2,4-DNP melted at 231.5–232.5° (lit.[8] 235–236°).

Registry No.—I, 88-26-6.

[5] M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1441 (1957).

[6] Courtesy of Dr. G. M. Coppinger.

[7] C. D. Cook, R. C. Woodworth, and P. Fiana, *J. Amer. Chem. Soc.*, **78**, 4159 (1956).

[8] T. W. Campbell and G. M. Coppinger, *ibid.*, **74**, 1469. (1952).

Isomerization of (−)-β-Pinene to High Optical Purity (−)-α-Pinene

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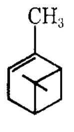
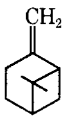
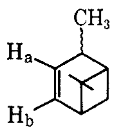
The recent work by Brown and coworkers[1] in the asymmetric synthesis of optically active alcohols has increased the need for a method to conveniently obtain high optical purity (−)-α-pinene[2] (I) in the laboratory. We encountered this need while utilizing Brown's procedure during the course of another investigation which required a rather large quantity of I.



I



II



III

The isomerization of (−)-β-pinene (II) to I has previously been carried out with rosin acid[3] or with palladium black saturated with hydrogen.[4,5] Although the palladium experiment realized nearly quantitative conversion of II to I, the optical yield, *i.e.*, conversion of optical activity to product, was only 82%. In addition, significant quantities of palladium are required to produce large amounts of I.

In view of the recent work in our laboratory and elsewhere in the area of olefin isomerizations with iron pentacarbonyl,[6] it was felt that a similar method might result in an improved synthesis of high optical purity I from II. We wish to report a very convenient method whereby large quantities of high optical purity I can be prepared from II utilizing the relatively inexpensive iron pentacarbonyl.

Isomerization of II, $[\alpha]^{26}\mathrm{D}$ −20.32° (neat) (89.5% optical purity),[7] with 20 mol % iron pentacarbonyl for 32 hr at 135° produces I, $[\alpha]^{26}\mathrm{D}$ −44.45° (neat) (86.7% optical purity),[8] in about 45% yield. This represents an optical yield of 96.9%. Essentially identical results were obtained when the experiment was performed utilizing 10–900 g of II. This is an improvement over the results of Richter and Wolff,[4] who isomerized II, $[\alpha]^{20}\mathrm{D}$ −21.6° (neat) (95.2% optical purity), with palladium black, previously saturated with hydrogen, to I, $[\alpha]^{20}\mathrm{D}$ −40.0° (neat) (78.1% optical purity).

Although smaller amounts of $Fe(CO)_5$ could be used with about equal yields, larger amounts facilitate the isomerization. This preparation allows a considerable amount of less volatile by-products to be produced; however, I is easily purified by distillation. No δ-pinene (III), which might be expected to result from further isomerization of I, could be detected.[9] The nmr spectrum of I exhibited methyl absorptions at τ 9.15 and 8.75 (singlets) and 8.37 (quartet), and a vinyl hydrogen multiplet at τ 4.85. The spectrum shows *no* absorption at τ 4.04, where H_b of III has been reported to absorb,[10] even at high amplitude.

The isomerization was easily followed utilizing gas–liquid partition chromatography (glpc) with a Carbowax column and noting the disappearance and resultant formation of II and I, respectively. Another, but less accurate, method is by observing the disappearance of the characteristic infrared absorption at 11.4 μ (877 cm^{-1}) of II and the corresponding appearance of an absorption at 12.7 μ (787 cm^{-1}) characteristic of I. By such means, it was noted that isomerization began after 20 hr and was complete in less than 32 hr.

Experimental Section

The F & M vapor phase chromatograph, Model 810, equipped with a flame ionization detector, was used for analytical purposes. Helium was used as the carrier gas, with a 3-m Carbowax 20 M on Chromosorb G column. Nuclear magnetic resonance spectra were run on a Varian A-60 and infrared spectra on a Perkin-Elmer Model 137. Melting points were obtained with a Thomas-Hoover capillary apparatus. (−)-β-Pinene was purchased from Aldrich Chemical Co. and iron pentacarbonyl from

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[1] H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 397 (1964).

[2] For a recent review of pinenes, see D. V. Banthorpe and D. Whittaker, *Chem. Rev.*, **66**, 643 (1966).

[3] R. N. Moore, C. Golumbic, and G. S. Fisher, *J. Amer. Chem. Soc.*, **78**, 1175 (1956).

[4] F. Richter and W. Wolff, *Chem. Ber.*, **59**, 1733 (1926).

[5] G. Widmark, *Acta Chem. Scand.*, **9**, 938 (1955).

[6] (a) F. G. Cowherd and J. L. von Rosenberg, *J. Amer. Chem. Soc.*, **91**, 2157 (1969); (b) W. T. Hendrix, F. G. Cowherd, and J. L. von Rosenberg, *Chem. Commun.*, 97 (1968); (c) G. F. Emerson and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 4591 (1962); (d) B. Fell, P. Krings, and F. Asinger, *Chem. Ber.*, **99**, 3688 (1966); (e) M. D. Carr, V. V. Kane, and M. C. Whiting, *Proc. Chem. Soc.*, 408 (1964); (f) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

[7] The highest reported value for (−)-β-pinene is $[\alpha]^{22}\mathrm{D}$ −22.7° (neat), purified from the silver complex (see ref 2).

[8] (a) The highest reported value for (−)-α-pinene is $[\alpha]^{20}\mathrm{D}$ −51.28°, purified through the nitroso chloride: F. H. Thruber and R. C. Thielke, *J. Amer. Chem. Soc.*, **53**, 1030 (1931); (b) R. N. McDonald and R. N. Steppel, *ibid.*, **91**, 782 (1969), report a new high value for (−)-α-pinene of $[\alpha]^{25}\mathrm{D}$ −54.9° (*c* 2.0, ethanol). The rotation of the α-pinene cited in this work is $[\alpha]^{26}\mathrm{D}$ −47.5° (*c* 2, ethanol), giving an optical purity of 86.5%, which compares well with the value obtained for the neat liquid based on the value reported by Thruber and Thielke for the neat liquid.

[9] Purity is >97% α-pinene, with <3% β-pinene as contaminate, as indicated by gas–liquid partition chromatography.

[10] G. Zweifel and C. C. Whitney, *J. Org. Chem.*, **31**, 4178 (1966). *cis*-δ-Pinene: τ 4.04 (m, H_b) and 4.6 (broad d, H_a); *trans*-δ-pinene: τ 4.04 (m, H_b) and 4.75 (broad d, H_a).