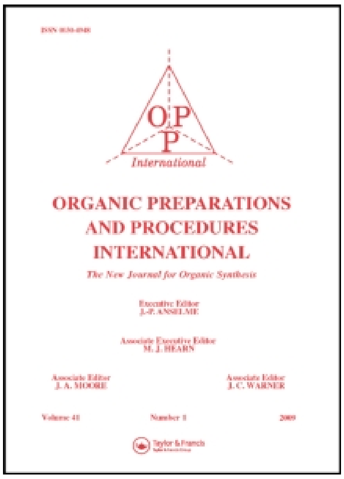

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

THE PREPARATION OF ALKYLPHENOLS USING *t*-BUTYL FUNCTION AS A POSITIONAL PROTECTIVE GROUP

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To cite this Article Tashiro, M. , Fukata, G. , Yamato, T. , Watanabe, H. , Oe, K. and Tsuge, O.(1976) 'THE PREPARATION OF ALKYLPHENOLS USING *t*-BUTYL FUNCTION AS A POSITIONAL PROTECTIVE GROUP', Organic Preparations and Procedures International, 8: 6, 249 — 262

To link to this Article: DOI: 10.1080/00304947609355638

URL: http://dx.doi.org/10.1080/00304947609355638

ORGANIC PREPARATIONS AND PROCEDURES INT. 8(6), 249-262 (1976)

THE PREPARATION OF ALKYLPHENOLS USING t-BUTYL FUNCTION AS A POSITIONAL PROTECTIVE GROUP[1]

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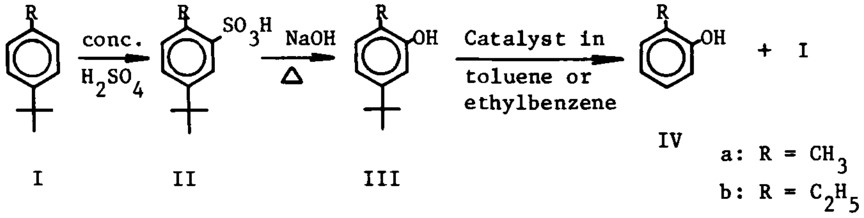
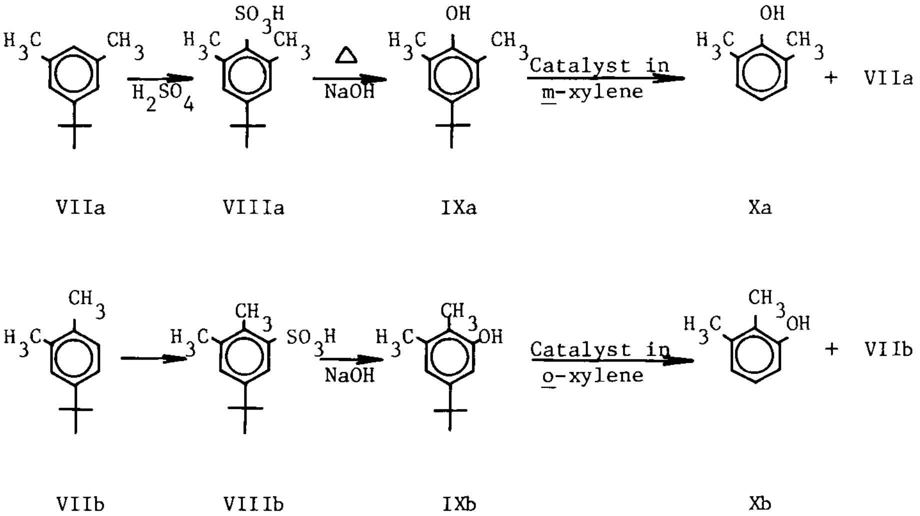
We reported previously that some halophenols[2], 2,2'-dihydroxydiphenylmethanes[3], dihydroxydiphenyls[4] and diaryl ether[5] were easily prepared by the $AlCl_3$-CH_3NO_2 or $AlCl_3$ catalyzed transalkylation of the corresponding t-butyl derivatives.



(1)

We report the selective preparation of o-alkylphenols(IV) and X by transalkylation of III and IX prepared as shown in equations 1 and 2. The structures of II were confirmed by conversion to the corresponding sulfonamides (VI) via the sulfonyl chloride (V). Gas chromatography of V indicated the presence of small amounts (23%) of the isomeric, 2-methyl- (Va') and 2-ethyl-4-t-butyl sulfonyl chloride (Vb'); the separation of V and V' by distillation was unsuccessful. These results suggest that II might also contain the isomeric sulfonic acids formed from the isomerization of II during the sulfonation of I with con. sulfuirc acid. However, the isolation of II′ and VI′ as well as V′ were unsuccessful. In this work, II, III and V were used without separation of II′, III′ and V′ respectively.



(2)

The reaction of IIa and IIb with a mixture of sodium hydroxide and potassium hydroxide were carried out at 300-330° for 30 min to afford the desired IIIa and IIIb with IIIa′ and IIIb′ in 76 and 42% yields respectively: the molar ratios of IIIa′/IIIa and IIIb′/IIIb are 17/83 and 25/75 mole/mole. The structure of IIIa′ was identified with authentic sample which was prepared by the t-butylation of o-cresol.[6]

On the other hand, when VIIa and VIIb were converted to 4-t-butyl-2,6-dimethyl- (IXa) and 5-t-butyl-2,3-dimethylphenol (IXb), no isomer formation was observed. The transalkylation of III and IX were carried out under various conditions and the results are summarized in Table 1.

Table 1.- The Transalkylation of III and IX with $AlCl_3$ [a)]

Substance	Solvent	Temp.(°C)	Product (%)	
IIIa	benzene	25	IVa(82)	Ic(80)
IIIa	toluene	25	IVa(80)	Ia(82)
IIIb	ethylbenzene	25	IVb(80)	Ib(80)
IXa	m-xylene	25	Xa(78)	VIIa(80)
IXb	o-xylene	25	Xb(82)	VIIb(81)

a) Reaction time was 3 hrs.

It should be noted that the separation of III and III′ is not necessary for the preparation of the desired IV, since the both III and III′ afforded same product IV.

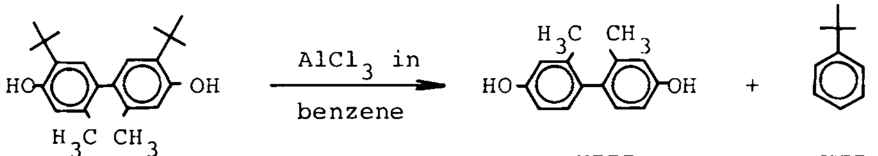
The $AlCl_3$ catalyzed transalkylation of 3,3′-di(t-butyl)-4,4′-dihydroxy- (XIIa), 3,3′-di(t-butyl-2,4′-dihydroxy- (XIIb) and 3,3′-di(t-butyl)-2,2′-dihydroxy-6,6′-dimethyldiphenyl (XIIc) prepared by the oxidative coupling of 6-t-butyl-3-methylphenol (XI) (see Table 2) afforded 4,4′-dihydroxy-2,2′-dimethyl- (XIIIa), 2,4′-dihydroxy-6,6′-dimethyl- (XIIIb) and 2,2′-dihydroxy-6,6′-dimethyldiphenyl (XIIIc). The VCl_4 and $VOCl_3$ catalyzed oxidative coupling of m-cresol afforded only XIIIa in trace amounts, but none of its isomers XIIIc which would also be expected to form in the reaction[7].

Table 2.- Oxidative Coupling XI[a)]

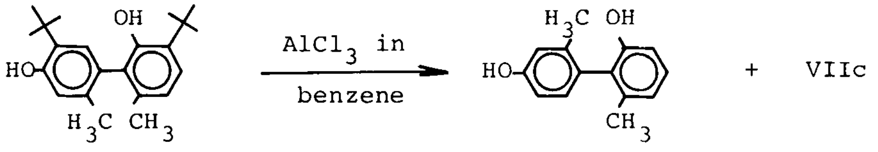
Reagents	Temp.(°C)	Yield(%)	Isomer Distribution (%) XIIa	 XIIb	 XIIc
chloroanil	160	25	34	50	16
VCl_4	20	18	89	11	0
VCl_4	0	29	97	3	0
$VOCl_3$	20	33	34	66	0

a) Reaction time was 1 hr.

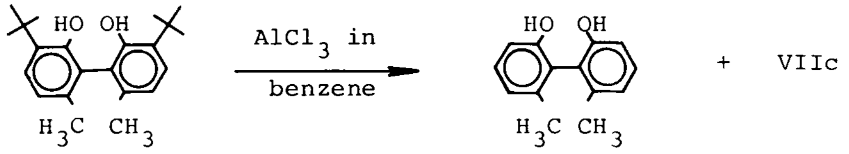
The structures of XIIa-XIIc were confirmed by their spectral data and the results of the transalkylation of XIIa-XIIc which



XIIa XIIIa VIIc



XIIb XIIIb



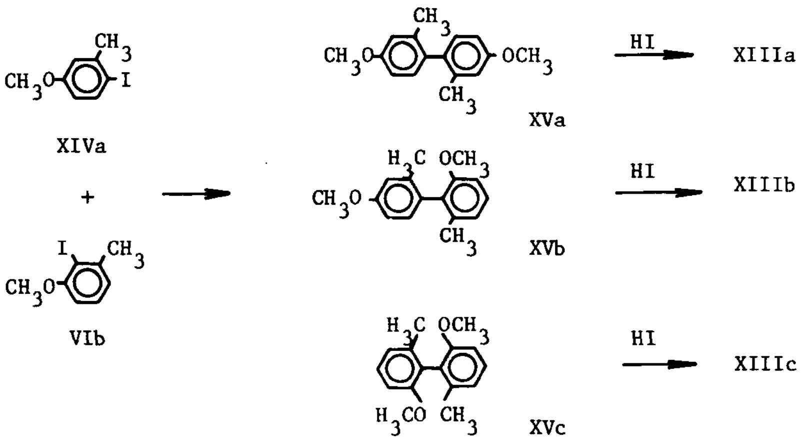
XIIc XIIIc

Table 3.- The $AlCl_3$ Catalyzed Transalkylation of XII in Benzene Solution[a)]

XII	Temp.(°C)	Time(min)	Product (%)
XIIa	20	15	XIIIa (70)
XIIb	50	60	XIIIb (76)
XIIc	50	60	XIIIc (70)

a) $AlCl_3$/XII : 2.2 mole/mole, Benzene/XII : 120 mole/mole.

will be described below. Identification of XIIIa and XIIIc were carried out by the comparison of thier IR spectra with those of the authentic samples which were prepared according to the reported method[10,11]. XIIIb was prepared by the cross Ullman reaction of XIVa and XIVb, which gave XVa, XVb and XVc: however, the isolation of XVb from the mixture of the products was not dificult since XVb was the main product.



EXPERIMENTAL

All melting and boiling points are uncorrected. IR spectra were measured as KBr pellets or liquid films on a Nippon Bunko IR-A spectrophotometer and NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with TMS as an internal standard. Mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet (ionization energy 70 eV).

Analytical Procedure.- The analyses were carried out by gas chromatography using a Yanagimoto Gas Chromatography, Yanaco YR-101; 30% high vacuum silicon grease, 75 cm; programmed temperature rise, 12 /min; carrier gas, helium, 25 ml/min. From the area of individual peaks, mole% figures were calculeted for each product.

Sulfonation of Ia.- To 250 g of conc. sulfuric acid was added gradually 74 g (0.5 mole) of Ia at room temperature. After the reaction mixture was stirred at 50° for 2 hr, it was poured into a large amount of ice, and to the solution was saturated sodium chloride. The precipitated colorless crystals was collected by filtration, washed with saturedted sodium chloride solution and dried *in vacuo* affording 120 g (77%) of sodium salt of IIa, mp 300°. NMR (D_2O) δ ppm: 1.25 (9H, s, $6\text{-}(C\underline{H}_3)_3$), 2.57 (3H, s, $C\underline{H}_3$) and 7.25-7.95 (3H, m, aromatic protons).

Sulfonation of Ib.- To 200 g of conc. sulfonic acid was added gradually 50 g (0.31 mole) of Ib at 25° in the period of 1 hr under stirring, and the stirring was continued for 6 hr longer. The reaction mixture was treated and worked up as described above affording 46.5 g (53%) of sodium salt of IIb, mp 300°.

Sulfonation of VIIa.- After 60 g of 5-t-butyl-m-xylene (VIIa) was added gradually into 240 g of conc. sulfuric acid at 25° over a period of 1 hr, the reaction mixture was stirred for 5 hr, and 100 ml saturated sodium chloride solution added, colorless crystals precipitated. The precipitate was collected and dried affording 97 g (76%) of sodium salt of 2,6-dimethyl-t-butyl sulfonic acid (VIIIa). VIIIa was used as a starting material for the preparation of 2,6-dimethyl-4-t-butylphenol (IXa).

Sulfonation of VIIIb.- Similarly 97 g of sodium salt of 2,3-doimethyl-5-t-butylsulfonic acid (VIIIb) was obtained by mean of sulfonation of 60 g of 5-t-butyl-o-xylene (VIIb) under some condition as described above.

Alkali Fusion of IIa.- After a mixture 100 g of sodium hydroxide and 40 g of potassium hydroxide was fused by heating, the alkaline mixture was cooled to 230°. To the alkaline mixture was added gradually 74 g of IIa at 230° in the period of 15 min. During the addition of IIa, the reaction temperature was increased to 270° from 230°. After addition of VIIIa, the reaction temperature was increased from 270° to 300-330° under stirring and the stirring was continued for 30 min. After the reaction mixture was cooled to room temperature, it was dissolved with 200 ml of water and 280 ml of diluted sulfuric acid (1:1) was added into the aqueous solution. Distillation with steam afforded 24 g of IIIa (containing IIIa′) as pale yellow liquid; bp 136-139°/13 mm. IR (KBr) cm^{-1}; 3360 (νOH). NMR (CCl_4) δ ppm; 1.20 (9H, s, $(C\underline{H}_3)_3$), 2.16 (3H, s, $C\underline{H}_3$), 5.85 (lH, s, $O\underline{H}$) and 6.50-7.10 (3H, m, aromatic protons).

The gas chromatography of the products indicated that the ratio of IIIa/IIIa′ was 17/83.

Alkali Fusion of IIb.- Similarly 40 g of IIb was treated and worked up as described above affording 7.85 g of mixture of IIIb and IIIb′ (25/75) as pale yellow liquid : bp 130-134°/15 mm.

Preparation of IXa.- After a mixture of 10 g of sodium hydroxide and 60 g of potassium hydroxide was fused by heating, the alkaline mixture was cooled at 230°. To the alkaline mixture was added gradually 50 g of VIIIa at 230° in the period of 15 min. During the addition of VIIIa, the reaction temperature was increased to 270° from 230°. After addition of VIIIa, the reaction temperature was increased from 270° to 300-330° with stirring which was continued for 30 min. After the reaction mixture had been cooled to room temperature, it was diluted with 200 ml of water and 280 ml of dilute sulfuric acid (1:1) was added into the aqueous solution. Distillation with steam afforded 7.54 g of IXa as colorless prisms, mp 72.5-73.5° (petroleum ether). IR (KBr) cm^{-1}: 3350 (νOH) and 2960 (νOH). NMR (CCl_4) δ ppm: 1.24 (9H, s, $(C\underline{H}_3)_3$), 2.18 (6H, s, $C\underline{H}_3$), 4.40 (lH, s, $O\underline{H}$), and 0.83 (2H, s, aromatic protons).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18.

Found: C, 80.59; H, 10.07.

Preparation of IXb.- Similarly 50 g of VIIIb was treated and worked up as described above to afford 14.6 g of IXb as colorless liquid, bp 143-146°/18 mm. IR cm^{-1}: 3360 (νOH) and 2960 (νOH). NMR (CCl$_4$) δ ppm: 1.20 (9H, s, $(C\underline{H}_3)_3$), 2.06 (3H, s, $C\underline{H}_3$), 2.20 (3H, s, $C\underline{H}_3$), 5.54 (1H, s, $O\underline{H}$), 6.50 and 6.63 (each 1H, s, aromatic protons).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18.
Found: C, 80.68; H, 10.23.

The Transalkylation of III.- a) *The AlCl$_3$Catalyzed Transalkylation of IIIa in Benzene*.- To a solution of 3.5 g (22.9 mmole) of IIIa in 150 g of benzene was added 7 g (52.6 mmole) of aluminum chloride at room temperature (25°C) with stirring which was continued for 3 hr. The reaction mixture was quenched with water and the organic layer was separated. The organic layer was extracted with 10% sodium hydroxide solution. The extract was acidified with 10% hydrochloric acid and extracted with diethyl ether. The ethereal solution was dried over sodium sulfate and evaporated *in vacuo* affording 2 g (82.3%) of IVa. Distillation of the residual organic layer from the extraction with 10% sodium hydroxide, gave 2.78 g (88%) of *t*-butyl benzene (Ic). b) *The AlCl$_3$ Catalyzed Transalkylation of IIIa in Toluene*.- To a solution of 4 g (24.4 mmole) of 4 g (24.4 mmole) of IIIa in 300 g of toluene was added 10 g (74 mmole) of AlCl$_3$ at 25° with stirring which was continued for 3 hrs. The reaction mixture was treated and worked up as described above affording 2.19 g (79%) of IVa and 2.95 g (80%). c) *The AlCl$_3$-CH$_3$NO$_2$ Catalyzed Transalkylation of IIIa in Toluene*.- Similarly a mixture of 2 g (12 mmole) of IIIa, 33.7 g

(317 mmole) of toluene and $AlCl_3$-CH_3NO_2 catalyst (2.88 g/5 ml) was treated at 50° and worked up as described above affording 0.33 g (25%) of IVa and 0.38 g (18.5%) of Ia. The unchanged IIIa was recovered in 71% yield. d) The $AlCl_3$-CH_3NO_2 Catalyzed Transalkylation of IIIb in Ethylbenzene.- Similarly a mixture of 2 g (11 mmole) of IIIb, 35.6 g (336 mmole) of ethylbenzene and $AlCl_3$-CH_3NO_2 catalyst (2.21 g/4.4 ml) was treated at 50° and worked up as described above affording 0.24 g (18%) of IVb and 0.38 g (21%) of Ib, and 1.3 g (65%) of IIb was recovered. e) The $AlCl_3$ Catalyzed Transalkylation of IIIb in Ethylbenzene.- A mixture of 2 g of IIIb, 35.6 g of ethylbenzene and 2.21 g (16.8 mmole) of aluminum chloride was treated and worked up as described above affording 1.07 g (80%) of IVb and 1.43 g (80%) of Ib.

Transalkylation of IXa. a) $AlCl_3$-CH_3NO_2 Catalyzed.- To a solution of 2 g (11 mmole) of IXa in 35.8 g (377 mmole) of *m*-xylene was added $AlCl_3$-CH_3NO_2 catalyst (2.2 g/4.4 ml). The reaction mixture was stirred at 50° for 3 hr, and it was poured into large amount of water. The organic layer was separated and the water layer was extracted with benzene. The organic layer and the benzene solution were combined and extracted with 50 ml of 10% sodium hydroxide solution. The extract was acidified with 10% hydroxhloric acid and extracted with ether. The ethereal solution was dried over sodium sulfate and evaporated *in vacuo* to afford 1.05 g (78%) of Xa; mp 41-42°, lit.[8], 47-48°. IR (KBr) cm^{-1}: 3380 (νOH). NMR (CCl_4) δ ppm: 2.19 (6H, s, $C\underline{H}_3$), 4.40 (1H, s, O$\underline{H}$), 6.50 (3H, m, aromatic protons). Distillation of the residual organic layer from the extraction with 10% sodium hydroxide, gave VIIa (80%).

b) $AlCl_3$ Catalyzed.- To a solution of 0.8 g (4.5 mmole) of IXa in 35.8 g of m-xylene was added 2 g of $AlCl_3$. After the reaction mixture was stirred at 25° for 3 hr, it was treated and worked up as described above affording 0.44 g (80%) of Xa and 0.36 g (78%) of VIIa.

The Transalkylation of IXb. a) $AlCl_3$-CH_3NO_2 Catalyzed.- To a solution of 2 g (11 mmole) of IXb in (377 mmole) of o-xylene was added $AlCl_3$-CH_3NO_2(2.2 g/4.4 ml). After the reaction mixture was stirred at 50° for 3 hrs, it was treated and worked up as described above affording 0.24 g (18%) of Xb and 0.12 g (6.7%) of VIIb. IVb: colorless prisms, mp 70-71°, lit.[9], mp 75°. IR (KBr) cm^{-1}: 3300 (νOH). NMR (CCl_4) δ ppm : 2.09 (3H, s, $C\underline{H}_3$), 2.20 (3H, s, $C\underline{H}_3$), 4.91 (1H, s, $O\underline{H}$) and 6.20-7.00 (3H, m, aromatic protons). b) $AlCl_3$ Catalyzed.- To a solution of 3 g of IXb in 51.7 g of o-xylene was added 6 g of $AlCl_3$. After the reaction mixture was stirred at 25° for 3 hrs, it was treated and worked up as described above affording 1.68 g (81.6%) of Xb and 2.21 g (80.7%) of VIIb.

Preparation of Va.- After mixture of 30 g of sodium salt of IIa and 30 g of PCl_5 was heated on a water bath (90-100°) for 30min, the reaction mixture was poured into ice-water and extracted with ether. The ethereal solution was dried over sodium sulfate and evaporated *in vacuo* to leave only resinous material which was distilled to afford 25 g of IVa as colorless liquid; bp 153-157°/20 mm. NMR ($CDCl_3$) δ ppm:1.35 (9H, s, $(C\underline{H}_3)_3$), 2.82 (3H, s, $C\underline{H}_3$), and 7.20-8.00 (3H, m, aromatic protons). The gas chromatography of the product indicated that Va and Va′ were formed in a ratio of 23/77.

Anal. Calcd for $C_{11}H_{15}SO_2Cl$: C, 53.50; H, 6.08.

Found: C, 53.48; H, 6.19.

Preparation of Vb.- Similarly a mixture of 30 g of sodium salt of IIb and 30 g of PCl_5 was treated and worked up as described above affording 2.6 g of IV as colorless liquid, mp 109-167°/20 mm. The ratio of Vb′/Vb as well as Va′/Va is 23/77.

Anal. Calcd for $C_{12}H_{17}O_2SCl$: C, 55.27; H, 6.57.

Found: C, 55.13; H, 6.50.

Preparation of VIa.- After a mixture of 1 g (41 mmole) of Va and 5 ml of conc. aqueous ammonium hydroxide was stirred for 1 hr, the reaction mixture was extracted with ether. The ethereal solution was dried over sodium sulfate and evaporated *in vacuo* to leave 0.95 g of colorless crystal which was recrystallized from benzene affording 0.7 g of VIa, as colorless plates, mp 142-143°.

Anal. Calcd for $C_{11}H_{17}NSO_2$: C, 58.15; H, 7.49; N, 6.17.

Found: C, 58.48; H, 7.11; N, 6.41.

Isolation of VIa′ which was also expected to form was unsuccessful.

Preparation of VIb.- Similarly 1 g (3.7 mmole) of VIb was treated and worked up as described above affording 0.6 g of VIb as colorless prisms, mp 114-118° (water-ethanol). Neither VIb′ nor VIa′ could be isolated.

Anal. Clacd for $C_{12}H_{19}NSO_2$: C, 59.71; H, 7.94.

Found: C, 59.75; H, 7.95.

Oxidative Coupling of XI with Chloroanil.- After a mixture of

20 g (122 mmoles) of XI and 15 g (60.5 mmoles) of chloroanil had been heated at 160° ± 5° for 1 hr, it was cooled to room temperature and extracted with 200 ml of petroleum ether (bp 60-85°) to afford 11 g of tetrachlorohydroquinone as residual substance. The petroleum ether solution was concentrated <u>in vacuo</u> to one-tenth of its volume and 1 g of chlorobenzene added as an internal standard for the gas chromatographic analyses. The yields given in Table 2 were calculated as described above. XIIa, XIIb and XIIc were isolated by the preparative gas chromatographic method respectively. XIIa: mp 205-207°, colorless prisms from petroleum ether; ir (KBr) 3550 cm^{-1} (OH); pmr ($CDCl_3$) δ 1.40 (18H, s, $(C\underline{H}_3)_3$), 1.98 (6H, s, $C\underline{H}_3$), 4.75 (2H, s, $O\underline{H}$), 7.00 and 7.35 (each 2H, s, aromatic protons).

<u>Anal</u>. Calcd for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26.

Found: C, 81.37; H, 9.54.

XIIb: mp 154-155°, colorless prisms from petroleum ether; ir (KBr) 3550 cm^{-1} (νOH)l; nmr ($CDCl_3$) δ 1.40 (18H, s, $(C\underline{H}_3)_3$), 1.90 (6H, s, $C\underline{H}_3$), 4.88 (2H, s, $O\underline{H}$), 6.60-7.26 (4H, m, aromatic protons).

<u>Anal</u>. Calcd for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26.

Found: C, 80.63; H, 9.35.

XIIc: mp 95=96°, colorless prisms from petroleum ether; ir (KBr) 3550 cm^{-1}; nmr ($CDCl_3$) δ 1.40 (18H, s, $(C\underline{H}_3)_3$), 1.90 (6H, s, $C\underline{H}_3$), 4.70 (2H, s, $O\underline{H}$), and 6.40-7.15 (4H, m, aromatic protons).

<u>Anal</u>.- Calcd for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26.

Found: C, 80.93; H, 9.54.

Oxidative Coupling of XI with VCl_4.- To a solution of 1 g of XI in 30 ml of carbon tetrachloride was added 1.5 g/10 ml of VCl_4-CCl_4 solution and the reaction mixture was stirred at 20° for 1 hr under stream of nitrogen, then it was quenched with 50% H_2SO_4. The organic layer was separated and the water layer was extracted with 20 ml of benzene; the benzene solution and the organic layer were combined and dried over sodium sulfate. The solution was worked up as described above affording XIIa and XIIb in the yields given in Table 2.

Oxidative Coupling of XI with $VOCl_3$.- Similiarly a solution of XI and 1.5 g of $VOCl_3$ in 50 ml of benzene was treated at 20° for 1 hr and worked up as described above to give XIIa and XIIb.

4,4'-Dihydroxy-2,2'-dimethyldiphenyl (XIIIa).- After a solution of 100 mg of XIIa and 91 mg of $AlCl_3$ in 3 ml of benzene was shaken at 20° for 15 min, it was quenched with 3 ml of 6N hydrochloric acid. The organic layer was separated and the water layer was extracted with ether and the ethereal solution was combined with the organic layer. The solution was combined and extracted with 10% NaOH solution (5ml x 3); the alkaline solution was acidified with 10% hydrochloric acid and extracted with ether (10 ml x 3). The ethereal solution was dried over sodium sulfate and evaporated *in vacuo* affording 50 mg (76%) of XIIIa, mp 98-100°, lit.[7], mp 115-116°, colorless prisms from chloroform; ir (KBr) 3100-3600 cm^{-1} (OH), mass spectrum: 214 m/e (M^+).

2,4'-Dihydroxy-6,2'-dimethyldiphenyl (XIIIb).- A solution of 100 mg of XIIb and 182 mg of $AlCl_3$ in 3 ml of benzene was treated at 50° for 1 hr and worked up as described above affording 46 mg (70%) of XIIIb as colorless liquid which was purified by the preparative gas chromatographic method. Ir (liquid film on NaCl plates) 3200-3580 cm^{-1} (OH); nmr ($CDCl_3$) δ 191 (6H, s, $C\underline{H}_3$), 5.40 (2H, s, $O\underline{H}$) and 6.50-7.30 (6H, m, aromatic protons) ; mass spectrum: 214 m/e (M^+).

2,2'-Dihydroxy-6,6'-dimethyldiphenyl (XIIIc).- Similarly a solution of 11 mg of XIIc and 91 mg of $AlCl_3$ in 3 ml of benzene was treated and worked up as described above affording 52 mg (79%) of XIIIc, mp 163-164°, lit.[10], mp 164°, colorless prisms from chloroform, ir (KBr) 3400-3500 cm^{-1} (OH); mass spectrum: 214 (M^+).

The Ullman Reaction of a Mixture of 2-Iodo-3-methoxy-1-methylbenzene and 2-iodo-5-methoxy-1-methlbenzene.- A mixture of 1 g of 2-iodo-3-methoxy-1-methylbenzene (XIVa),[10] 1 g of 2-iodo-5-methoxy-1-methylbenzene (XIVb)[11] and small amount of copper powder was heated at 230°, an additional 2 g of copper powder was added in period of 30 min then it was heated at 270° for 15 min. The reaction mixture cooled to room temperature was extracted with benzene. The three products XVa, XVb and XVc were isolated from the benzene solution by using preparative gas chromatographic method. The both products, XVa and XVc, were also prepared by the Ullman reaction of the corresponding XIVa and XIVc respectively, so XVb should be 2,2'-dimethyl-4,6'-dimethyldiphenyl. The treatment of XVa-XVc with hydroiodic acid (d: 1.7) under conditions usually used afforded XIIIa-XIIIc in good yields respectively.

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(Received Sept. 3, 1976; in revised form Dec. 9, 1976)