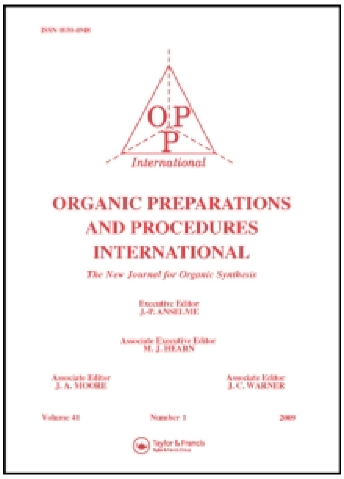

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STUDIES ON POSITIONAL PROTECTIVE GROUPS ON AROMATIC RINGS II. A NEW PREPARATIVE METHOD FOR DIHYDROXYDIPHENYLS WITH t-BUTYL GROUP AS A PROTECTIVE GROUP.[1]

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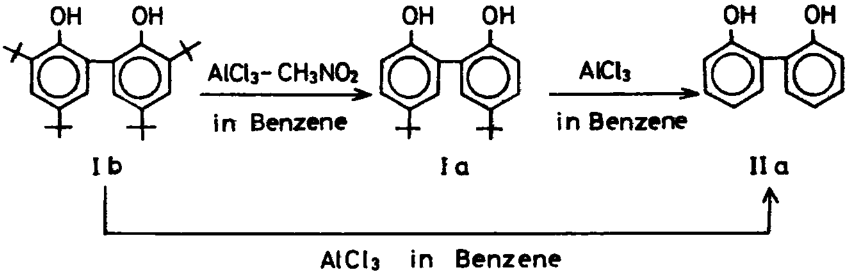
Previously, it was reported[1] that some halophenols were easily prepared by the transalkylation reactions of the corresponding benzyl- or t-butylhalophenols catalyzed by aluminum chloride or aluminum chloride-nitromethane catalyst and that the t-butyl group was preferable than the benzyl group. The present investigation was undertaken to determine if the t-butyl group could serve as a positional protective group for the preparation of dihydroxydiphenyls. The present paper describes the transalkylation of 5,5'-di(t-butyl)-2,2'-di-



dihydroxy- (Ia), 3,3',5,5'-tetra(t-butyl)-2,2'-dihydroxy- (Ib), 3,3',5,5'-tetra(t-butyl)-4,4'-dihydroxy- (Ic), and 5,5'-di-(t-butyl)-3,3'-dimethyl-2,2'-dihydroxydiphenyl (Id) under various conditions and the results are summarized in Table 1.

Table 1. The $AlCl_3$ and $AlCl_3$-CH_3NO_2 Catalyzed Transalkylation of I in Benzene.[a]

Run	I	Catalyst[b]	Catalyst/I (mol/mol)	Time (min)	Product (%)[c]
1	a	B	4.0	60	0[d]
2	a	A	4.0	60	IIa (65)
3	b	B	4.0	60	Ia (72)
4	b	A	4.0	15	IIa (73)
5	c	B	2.2	30	IIb (82)
6	d	A	2.2	60	IIc (83)

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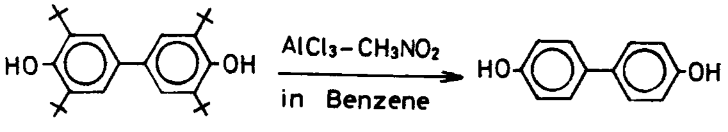
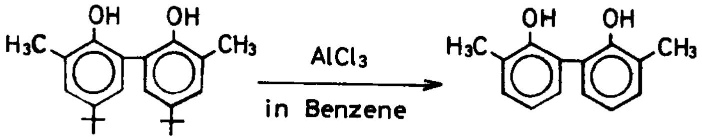
a) Benzene/I = 120 mole/ 1 mole; Temperature is 50° unless otherwise noted. b) A: $AlCl_3$; B: $AlCl_3$-CH_3NO_2. c) The yields of product were determined by the gas chromatographic analyses. d) Ia was almost quantatively recovered. e) Temp.: 30°.

Table 1 shows that the transalkylation reaction of Ia did not occur with $AlCl_3$-CH_3NO_2 as catalyst which is an active for the transalkylation of t-butylhalophenols.[1] However, in the presence of $AlCl_3$, the expected 2,2'-dihydroxydiphenyl (IIa) was formed in good yield (Run 2). In addition, Ia and IIa were obtained from Ib in the presence of $AlCl_3$-CH_3NO_2 and $AlCl_3$ respectively (Runs 3 and 4).

However, runs 5 and 6 indicate that all four t-butyl group of Ic were easily transferred to benzene used as a solvent to afford IIb even with $AlCl_3$-CH_3NO_2 as catalyst and that the expected IIc was obtained from Id in the presence of $AlCl_3$ in good yield.



Ic IIb



Id IIc

The above results recommend this reaction as a more convenient preparation than the previously reported methods.[2-6]

EXPRIMENTAL

All mp. are uncorrected. IR spectra were measured as KBr pellets on a Nippon Bunko IR-S spectrophotometer and mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet (ionization energy 70 eV). NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with TMS as an internal reference.

Marerials.- 3,3',5,5'-Tetra(t-butyl)-2,2'-dihydroxy- (Ib), and 3,3',5,5'-tetra(t-butyl)-4,4'-dihydroxydiphenyl (Ic) were prepared by reported methods and purified by recrystallization: Ib: mp. 195-196°, lit.[3] mp. 196-198°, Ic: 184-185°, lit.[7] mp. 185°. 5,5'-Di(t-butyl)-2,2'-dihydroxy- (Ia), and 5,5'-di-(t-butyl)-3,3'-dimethyl-2,2'-dihydroxydiphenyl (Id) were obtained by oxidative coupling using VCl_4.[2]

Preparation of Ia and Ib.- A solution of 7.8g of VCl_4 in 30 ml of carbon terachloride was gradually added to a solution of 6.0g of 4-t-butylphenol in 150 ml of carbon tetrachloride at room temperature, the reaction mixture was stirred for 1 hr under a stream of nitrogen and then depomposed with 100 ml of 50% sulfuric acid. The carbon tetrachloride layer was separated and evaporated *in vacuo* to leave a residue, which was washed with 50 ml of petroleum ether (bp. 40-65°). The insoluble solid was recrystallized from petroleum ether (bp. 50-85°) to afford Ia (1.2g, 20%), mp. 204-205°, as colorless needles.

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78.
Found: C, 80.39; H, 8.92.

IR cm^{-1}: 3200 ($^{\nu}OH$). Mass spectrum m/e: 298 (M^+).

NMR ($CDCl_3$) δ ppm: 1.37 (18H, s, $(CH_3)_3C$), 6.90-7.10 (8H, m, aromatic protons and OH).

Ib was prepared as described above from 4-t-butyl-2-methylphenol[8]. Recrystallization of the crude product from petroleum ether (bp. 40-65°) afforded Id (1.98g, 30%), mp. 112-123°, as colorless prisms.

Anal. Calcd. for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26.
Found: C, 80.85; H, 9.43.

IR cm^{-1}: 3200-3500 ($^{\nu}OH$). Mass spectrum m/e: 326 (M^+).

NMR ($CDCl_3$) δ ppm: 1.12 (18H, s, $(CH_3)_3C$), 2.12 (6H, s, CH_3), 4.82 (2H, s, OH), 6.75-7.09 (4H, m, aromatic protons).

Aluminum chloride was purified by sublimation just prior to use and the aluminum chloride-nitromethane catalyst was prepared by the reported method.[9]

Analytical Procedure.- The quantitative estimations were carried out by gas chromatogrsphy using a Yanagimoto Gas Chromatography, Yanaco YR-101: column, 30% high vacuum silicon grease, 75 cm; programmed temperature rise, 12°/min; carrier gas, hyrogen, 30 ml/min.

From the areas of individual peaks, mole % figures were calculated for each product after the relative response data had been determined by the internal standard method; nitrobenzene was used as an internal standard substance.

General Procedures.- A mixture of 120 ml of benzene, 2,2-4.0 equivalent of the catalyst per mole of I and one mole of I was reacted and worked up as previously described.[1]

After the analyses, the ethereal solution was evaporated *in vacuo* to afford the crude product.

2,2'-Dihydroxydiphenyl (IIa), mp. 110-111°, lit.[10] mp. 109°, colorless needles from petroleum ether (bp. 40-65°).

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41.

Found: C, 77.53; H, 5.49.

4,4'-Dihydroxydiphenyl (IIb), mp. 274-275°, lit.[2] mp. 272°, colorless prisms from methanol.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41.

Found: C, 77.38; H, 5.21.

3,3'-Dimethyl-2,2'-dihydroxydiphenyl (IIc), mp. 81-82°, lit.[12] mp. 89°, colorless needles from petroleum ether (bp. 40-65°).

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59.

Found: C, 78.46; H, 6.56.

The practical yields of II were almost same as the data given in Table 1, which were determined by gas chromatographic analyses.

The spectroscopic data were in agreement with the assigned structures.

REFERENCES

* To whom inquiries should be present.

1. Part I of this series. see M. Tashiro, H. Watanabe and O. Tsuge, Org. Prep. Proced. Int., 6, 107 (1974).
2. W. L. Carrick, G. L. Karapinka and G. T. Kwiatowski, J. Org. Chem., 34, 2388 (1969).
3. H.-D. Becker, ibid., 34, 1198 (1969).
4. P. E. Fanta, Chem. Revs., 38, 139 (1946).
5. C. Haeusermann and H. Teichmann, Ber., 27, 2107 (1894).
6. G. Schulz and W. Kohlaus, ibid., 39, 3343 (1906).
7. M. S. Kharasch and B. S. Joshi, J. Org. Chem., 22, 1439 (1957).
8. A. Chichibabin, Compt. Rend., 198, 1239 (1934).
9. O. Tsuge, M. Tashiro and A. Torii, Kogyo Kagaku Zasshi, 70, 2287 (1967); C.A., 68, 104300 (1968).
10. H. Limpricht, Ann., 261, 332 (1891).
11. Y. Sugii and H. Shindo, Yakugaku Zasshi, 54, 826 (1934); C.A., 29, 790 (1935).

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