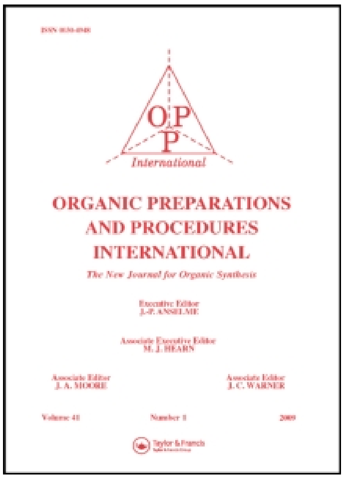

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STUDIES ON POSITIONAL PROTECTIVE GROUPS. IV. A NEW PREPARATIVE METHOD FOR DIHYDROXYDIPHENYLMETHANES WITH THE *T*-BUTYL GROUP AS A PROTECTIVE GROUP

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STUDIES ON POSITIONAL PROTECTIVE GROUPS. IV. A NEW PREPARATIVE METHOD FOR DIHYDROXYDIPHENYLMETHANES WITH THE t-BUTYL GROUP AS A PROTECTIVE GROUP.[1]

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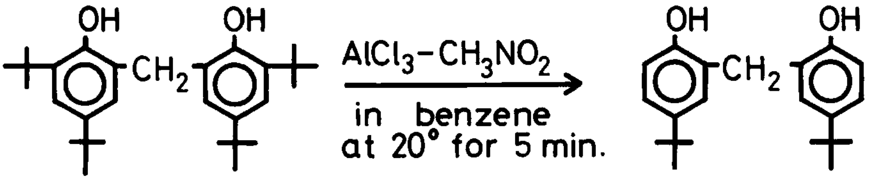
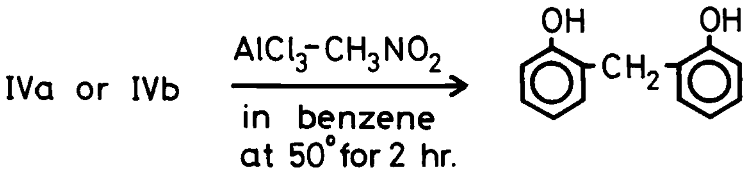
It has been previously reported that a t-butyl group of t-butylhalophenols is easily transferred to benzene used as a solvent to give the corresponding halophenols and t-butylbenzene even under the influence of a mild catalyst such as aluminum chloride-nitromethane ($AlCl_3$-CH_3NO_2) which did not



IVa

IVb



Va

catalyze the transbenzylation reaction of diphenylmethane.[2] This result seemed to strongly suggest that the t-butyl group might serve as a protective group for the preparation of some diphenylmethanes.

In the $AlCl_3$-CH_3NO_2 catalyzed transalkylation reaction of 3,3′,5,5′-tetra(t-butyl)-2,2′-dihydroxydiphenyl (I), it was also found that only t-butyl groups in the ortho position of I were easily transferred to benzene to yield 2,2′-dihydroxy-5,5′-di(t-butyl)diphenyl (II) and t-butylbenzene.[3] On the other hand, a stronger catalyst such as $AlCl_3$ had to be used to prepare 2,2′-dihydroxydiphenyl (III) from I or II by the transalkylation reaction. Owing to our interest in the preparation of dihydroxydiphenylmethanes by use of t-butyl protective group and in the relative ease of the transalkylation, we have studied the $AlCl_3$-CH_3NO_2 catalyzed transalkylation reactions of 3,3′,5,5′-tetra-t-butyl- (IVa), 5,5′-di(t-butyl)- (IVb), 3,3′-di(t-butyl)-5,5′-dimethyl- (IVc), 3,3′-dimethyl-5,5′-di(t-butyl)- (IVd) and 5,5′-di(t-butyl)-3,3′-dibromo-2,2′-dihydroxydiphenylmethane (IVe). The results are summarized in Table 1.

These results indicate that the ortho-t-butyl groups of I and of IV could be transferred more easily than the para-t-butyl groups. Furthermore, the para-t-butyl groups of IVa, IVb and IVe could be transferred by the mild $AlCl_3$-CH_3NO_2 catalyst which did not effect the transalkylation of para-t-butyl groups of I and II. These results recommend this reaction as a more convenient preparation for Va[4], Vb[5], Vd[6] and IVb[7].

Table 1. The $AlCl_3$-CH_3NO_2 Catalyzed Transalkylation of IV in benzene.[a]

Run	IV	Time	Temp.(°C)	Product (%)
1	a	5 min	20	IVb (80)
2	a	2 hr	50	Va (60)
3	b	2 hr	50	Va (85)
4	c	5 min	20	Vb (85)
5	d	2 hr	50	Vc (0)[b]
6	e	2 hr	50	Vd (41)

a : Benzene/IV = 50 ml/ 10 mmoles; Catalyst/IV = 2.2 moles/1 mole.

b : IVd was quantitatively recovered.

EXPERIMENTAL

General Experimental. All melting points are uncorrected. IR spectra were measured as KBr pellets 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 reference.

Materials. 3,3′,5,5′-Tetra(t-butyl)-2,2′-dihydroxy- (IVa), 3,3′-di(t-butyl)-5,5′-dimethyl-2,2′-dihydroxy- (IVc), 5,5′-di(t-butyl)-3,3′-dimethyl-2,2′-dihydroxy- (IVd) and 3,3′-dibromo-5,5′-di(t-butyl)-2,2′-dihydroxydiphenylmethane (IVe) were prepared by reported methods. IVa : mp. 145-146°, lit.[8] mp. 145-146°; IVc : mp. 132-134°, lit.[9] mp. 132-134°; IVd : mp. 140-141°, lit.[9] mp. 140-141°; IVe : mp. 136.5-138°, lit.[9] mp. 136.5-138°.

Aluminum chloride was purified by sublimation just prior to use and aluminum chloride-nitromethane catalyst was prepared as reported previously.[10]

2,2'-Dihydroxydiphenylmethane (Va).

a) From IVa.- A mixture of 4.24 g (10 mmoles) of IVa, 50 ml of benzene and $AlCl_3$-CH_3NO_2 (3 g/6 g) catalyst was shaken at 50° for 120 min and the reaction mixture was then quenched with 10% hydrochloric acid. After the organic layer was separated and dried over sodium sulfate, the solvent was evaporated *in vacuo*. The residue was chromatographed on silica-gel using benzene and diethyl ether as the eluent to give 3.67 g (69%) of *t*-butylbenzene (form the benzene elution) and 1.2 g (60%) of Va (from the diethyl ether elution), mp. 118-119°, lit.[4] mp. 118-119°, colorless prisms from petroleum ether (bp. 40-65°); ir(KBr) 3300 cm^{-1}(OH), pmr ($CDCl_3$) δ 3.91 (s, 2, CH_2), 6.69-7.41 (m, 8, aromatic protons) and 7.55 (broad s, 2, OH).

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04.

Found: C, 78.11; H, 5.78.

b) From IVb.- After a mixture of 0.312 g (1 mmole) of IVb, 5 ml of benzene and $AlCl_3$-CH_3NO_2 (0.3 g/ 0.6 g) catalyst was shaken at 50° for 2 hr, the reaction mixture was treated and worked up as described above, affording 0.17 g (85%) of Va.

5,5'-Di(t-butyl)-2,2'-dihydroxydiphenylmethane (IVb).- After a mixture of 4.24 g (10 mmoles) of IVa, and 50 ml of benzene and $AlCl_3$-CH_3NO_2 (3 g/ 6 g) was shaken at 20° for 5 min, the reaction mixture was treated and worked up as described above, affording 2.7 g (almost quantative yield) of *t*-butylbenzene and 2.52 g (80%) of IVb, mp. 156-157°, lit.[7] mp. 156°, colorless prisms from a mixed solvent of petroleum ether and diethyl ether (1:1); ir(KBr) 3260 cm^{-1} (OH), pmr($CDCl_3$) δ 1.24 (s, 18, t-CH_3), 3.89 (s, 2, CH_2), 6.62-7.35 (m, 6, aromatic protons) and 7.52 (s, 2, OH).

Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03.
Found: C, 80.36; H, 8.93.

IVb was reacted with bromine in methanol to give IVd quantitatively.

5,5'-Dimethyl-2,2'-dihydroxydiphenylmethane (Vb).- After a mixture of 3.40 g (10 mmoles) of IVc, 50 ml of benzene and $AlCl_3$-CH_3NO_2 (3 g/6 g) catalyst was shaken at 20° for 5 min, the reaction mixture was treated and worked up as described above giving 2.0 g of t-butylbenzene and 1.94 g (85%) of Vb, mp. 127-128°, lit.[5] 126°, colorless needles from petroleum ether; ir(KBr) 3260 cm^{-1} (OH); pmr($CDCl_3$) δ 2.22 (s, 6, CH_3), 3.81 (s, 2, CH_2), 6.58-7.18 (m, 6, aromatic protons) and 7.53 (broad s, 2, OH).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06.
Found: C, 78.96; H, 6.98.

3,3'-Dibromo-2,2'-dihydroxydiphenylmethane (Vd).- A mixture of 0.94 g (2 mmoles) of IVe, 10 ml of benzene and $AlCl_3$-CH_3NO_2 (o.6 g/ 1.2 g) was shaken at 50° for 2 hr, and then the reaction mixture was treated and worked up as described above affording 0.29 g (41%) of Vd, mp. 96-97°, lit.[6] mp. 96°, colorless needles from petroleum ether; ir(KBr) 3500 and 3480 cm^{-1}; pmr($CDCl_3$) δ 4.03 (s, 2, CH_2), 5.98 (s, 2, OH) and 6.59-7.45 (m, 6, aromatic protons).

Anal. Calcd for $C_{13}H_{10}O_2Br_2$: C, 43.61; H, 2.82.
Found: C, 43.51; H, 2.82.

REFERENCES

1. For part III, see M. Tashiro, H. Watanabe and O. Tsuge, Org. Prep. Proced. Int., 7, 43 (1975).
2. M. Tashiro, H. Watanabe and O. Tsuge, ibid., 6, 117 (1974).
3. M. Tashiro, H. Watanabe and O. Tsuge, ibid., 6, 107 (1974).
4. S. Seto and H. Horiuchi, Kogyo kagaku Zasshi, 56, 890 (1953); C.A., 49, 6889e (1955).
5. M. Koebner, Angew. Chem., 46, 251 (1933).
6. W. Lotz and V. Bohmer, Makromol. Chem., 148, 61 (1971).
7. A. Zinke, R. Kretz, E. Leggemie and K. Hossinger, Monatsh. Chem., 83, 1213 (1952).
8. R. Wegler and K. Faber, Chem. Ber., 82, 327 (1949).
9. M. Tashiro, G. Fukata and K. Oe, Sei-Ken Hokoku (The Reports of Research Institute of Industrial Science, Kyushu University) in press.
10. O. Tsuge, M. Tashiro and A. Torii, Kogyo Kagaku Zasshi, 70, 2287 (1967); C.A., 68, 104300 (1968).

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