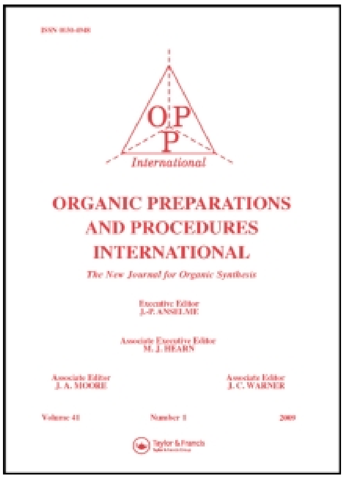

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STUDIES ON POSITIONAL PROTECTIVE GROUPS. VII. A NEW PREPARATIVE METHOD FOR 2,2'-DIHYDROXYDIPHENYLMETHANES WITH THE CHLORO OR BROMO GROUPS AS A PROTECTIVE GROUP

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STUDIES ON POSITIONAL PROTECTIVE GROUPS. VII. A NEW PREPARATIVE METHOD FOR 2,2'-DIHYDROXYDIPHENYLMETHANES WITH THE CHLORO OR BROMO GROUPS AS A PROTECTIVE GROUP.[1]

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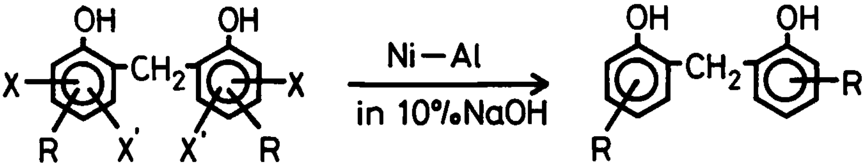
It was previously reported that 4,4'-dihydroxydiphenylmethanes were easily prepared by the reductive dehalogenation reactions of corresponding halo-4,4'-dihydroxydiphenylmethanes.[1] This paper reports the preparation of some 2,2'-dihydroxydi-



I

II

a : R = H, X = X' = Cl (3,3',5,5'-)
b : R = H, X = X' = Br (3,3',5,5'-)
c : R = Me (3,3'-), X = Cl (5,5'-),
X' = H
d : R = Me (4,4'-),
X = X' = Cl (3,3',5,5'-)
e : R = t-Bu (5,5'-),
X = Br (3,3'-), X' = H

a : R = H
b : R = Me (3,3'-)
c : R = Me (4,4'-)
d : R = t-Bu (5,5'-)

phenylmethanes (II) by the reductive dehalogenation reaction of the corresponding halo-2,2'-dihydroxydiphenylmethanes (I).

The reductive dehalogenation of 3,3',5,5'-tetrachloro- (Ia), 3,3',5,5'-tetrabromo- (Ib), 5,5'-dichloro-3,3'-dimethyl- (Ic), 3,3',5,5'-tetrachloro-4,4'-dimethyl- (Id) and 3,3'-dibromo-5,5'-di(t-butyl)-2,2'-dihydroxydiphenylmethane (Ie) was carried out in 10% sodium hydroxide solution with Raney Ni-Al alloy. The results are summarized in Table 1.

Table 1. The Dehalogenation reactions of Halo-2,2'-dihydroxydiphenylmethanes (I) in 10% NaOH Solution with Raney Ni-Al Alloy.

Run	I	Time(min)	Temp.(°C)	Product, II (%)
1	a	30	95-97	a (51)
2	b	10	rt	a (64.5)
3	c	120	95-97	b (50)
4	d	60	95-97	c (87)
5	e	180	95-97	d (0)[a]

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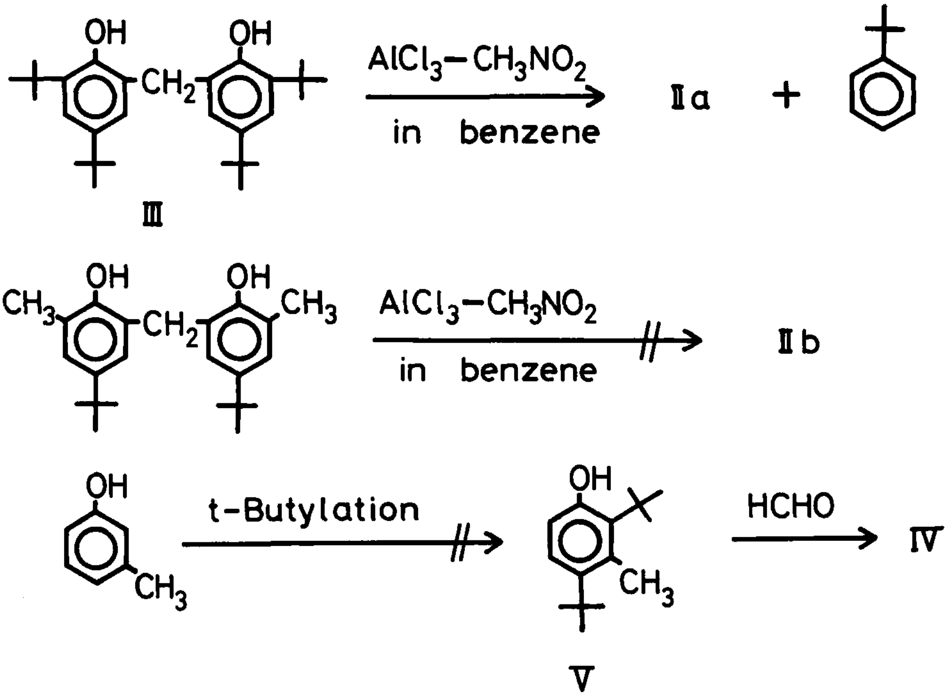
a) Ie was almost quantitatively recovered.

As Table 1 shows, the expected 2,2'-dihydroxy- (II a), 2,2'-dihydroxy-3,3'-dimethyl- (II b) and 2,2'-dihydroxy-4,4'-dimethyldiphenylmethane (II c) were obtained but not 2,2'-dihydroxy-5,5'-di(t-butyl)diphenylmethane (II d). Probably the above result might be due to the insolubility of II d into the 10% sodium hydroxide solution containing small amount of ethanol.

Although II a could be prepared by the transalkylation of 3,3',5,5'-tetra(t-butyl)-2,2'-dihydroxydiphenylmethane (III), II b could not be synthesized by this method as previously reported.[2]

Also II c might be prepared from the corresponding t-butyl-derivate (IV) by the application of the transalkylation because the preparation of the starting material, 2,4-di(t-butyl)-m-cresol (V) of IV is very difficult.



The above results suggest this method as the most practical one for the preparation of II b and II c.

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 NMR spectrometer R-20 with TMS as an internal reference.

Materials. The preparations of 3,3',5,5'-tetrachloro- (Ia), 3,3',5,5'-tetrabromo- (Ib), 5,5'-dichloro-3,3'-dimethyl- (Ic), 3,3',5,5'-tetrachloro-4,4'-dimethyl (Id) and 3,3'-dibromo-5,5'-di(t-butyl)-2,2'-dihydroxydiphenylmethane (Ie) were previously reported.[3]

2,2'-Dihydroxydiphenylmethane (II a). From Ia.- To a solution of 1 g (2.96 mmoles) of Ia in 50 ml of 10% sodium hydroxide was gradually added 1 g of Raney Ni-Al alloy at room temperature and the reaction mixture was heated on a water bath (at 95-97°) for 30 min, and then it was cooled to room temperature. An insoluble substance was filtered and the filtrate was acidified with a 10% hydrochloric acid affording 0.3 g (51%) of II a, mp. 118-119°, lit.[1] mp. 118-119°, colorless prisms from petroleum ether (bp. 40-65°).

From Ib.- To a solution of 1 g (1.94 mmoles) of Ib in 50 ml of 10% sodium hydroxide was gradually added 1 g of Raney Ni-Al alloy over a period of 20 min without heating. The reaction mixture was worked up as described above affording 0.25 g (64.5%) of II a.

2,2'-Dihydroxy-3,3'-dimethyldiphenylmethane (II b).- To a solution of 2.97 g (10 mmoles) of Ic in 50 ml of 10% sodium hydroxide was gradually added 3 g of Raney Ni-Al alloy and the reaction mixture was heated on a water bath (at 95-97°) for 1 hr, and then additional 2 g of the alloy was added and the reaction mixture was further heated for 1 hr. After an insoluble substance was filtered, the filtrate was acidified with 10% hydrochloric acid and extracted with a 50 ml of ether. The ethereal layer was dried over sodium sulfate and evaporated *in vacuo* to give resinous materials which were chromatographed on silica-gel with benzene affording 1.15 g (50%) of II b, mp. 126-127°, as colorless needles from petroleum ether (bp. 65-80°).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06.
Found: C, 78.97; H, 7.06.

IR cm^{-1}: 3280 (νOH); NMR($CDCl_3$) δ ppm: 2.17 (s, 6H, C$\underline{H}_3$), 3.89 (s, 2H, C$\underline{H}_2$), 6.2 (broad s, 2H, O$\underline{H}$) and 6.5-7.2 (m, 6H, aromatic protons).

2,2'-Dihydroxy-4,4'-dimethyldiphenylmethane (II c).- To a solution of 1 g (2.73 mmoles) of Id in 50 ml of 10% sodium hydroxide and 10 ml of ethanol was added 1 g of Raney Ni-Al alloy and the reaction mixture was heated on a water bath (at 95-97°) for 30 min. Then an additional 1 g of the alloy was added and the whole mixture was heated a further 30 min and worked up as descirbed in case of II a affording 0.54 g (87%) of II c, mp. 132-134° as colorless needles from benzene.

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06.
Found: C, 78.60; H, 6.98.

IR cm^{-1}: 3280 (νOH); NMR(DMSO-d_6) δ ppm: 2.18 (s, 6H, C$\underline{H}_3$), 3.28 (s, 2H, C$\underline{H}_2$), 6.48(d, 2H, Jab = 7.5 cps, aromatic protons), 6.60 (s, 2H, aromatic protons), 6.78 (d, 2H, Jab = 7.5 cps, aromatic protons) and 9.10 (broad s, 2H, O$\underline{H}$).

Attempt to prepare of 2,2'-dihydroxy-5,5'-di(t-butyl)diphenylmethane (II d).- The reductive dehalogenation of Ie did not take place in 10% sodium hydroxide solution containing a small amount of ethanol to aid the solubility of Ie under the conditions shown in Table 1, but only starting material Ie was almost quatitatively recovered.

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* To whom inquiries sould be sent.

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