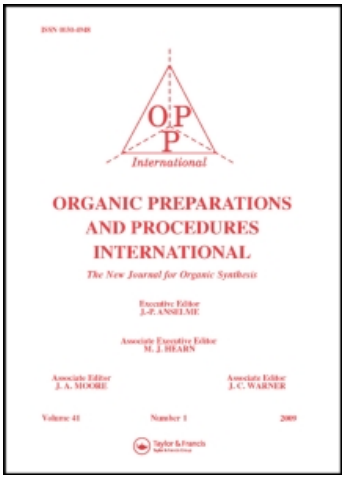

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STUDIES ON POSITIONAL PROTECTIVE GROUPS. V. A NEW PREPARATIVE METHOD FOR 4,4'-DIHYDROXY DIPHENYLMETHANES WITH THE CHLORO OR BROMO GROUPS AS A PROTECTIVE GROUP

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STUDIES ON POSITIONAL PROTECTIVE GROUPS. V. A NEW PREPARATIVE METHOD FOR 4,4'-DIHYDROXYDIPHENYLMETHANES WITH THE CHLORO OR BROMO GROUPS AS A PROTECTIVE GROUP.[1]

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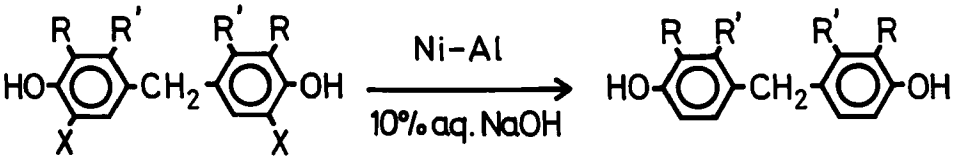
The preparation of 2,2'-dihydroxydiphenylmethanes by the aluminum chloride-nitromethane catalyzed transalkylation of the corresponding t-butyldihydroxydiphenylmethanes has been reported.[1] However, 4,4'-dihydroxydiphenylmethanes could not be prepared by a similar manner since the expected transalky-



I II

a: R = X = Br, R' = H

b: R = CH_3, X = Cl, R' = H

c: R = X = Cl, R' = CH_3

a: R = R' = H

b: R = CH_3, R' = H

c: R = H, R' = CH_3

lation reaction was accompanied by complex side-reactions.[2] It is well known that same halophenols can be dehalogenated by using suitable reductive reagents to yield the corresponding phenols.[3-6] We now describe the preparation of several 4,4'-dihydroxydiphenylmethanes by the dehalogenation of the corresponding halogen substituted compounds.

The dehalogenation of 3,3',5,5'-tetrabromo- (Ia), 5,5'-dichloro-3,3'-dimethyl- (Ib) and 3,3',5,5'-tetrachloro-2,2'-dimethyl-4,4'-dihydroxydiphenylmethane (Ic) which could be easily prepared from corresponding halophenols and 37% formalin were carried out under conditions shown in Table 1.

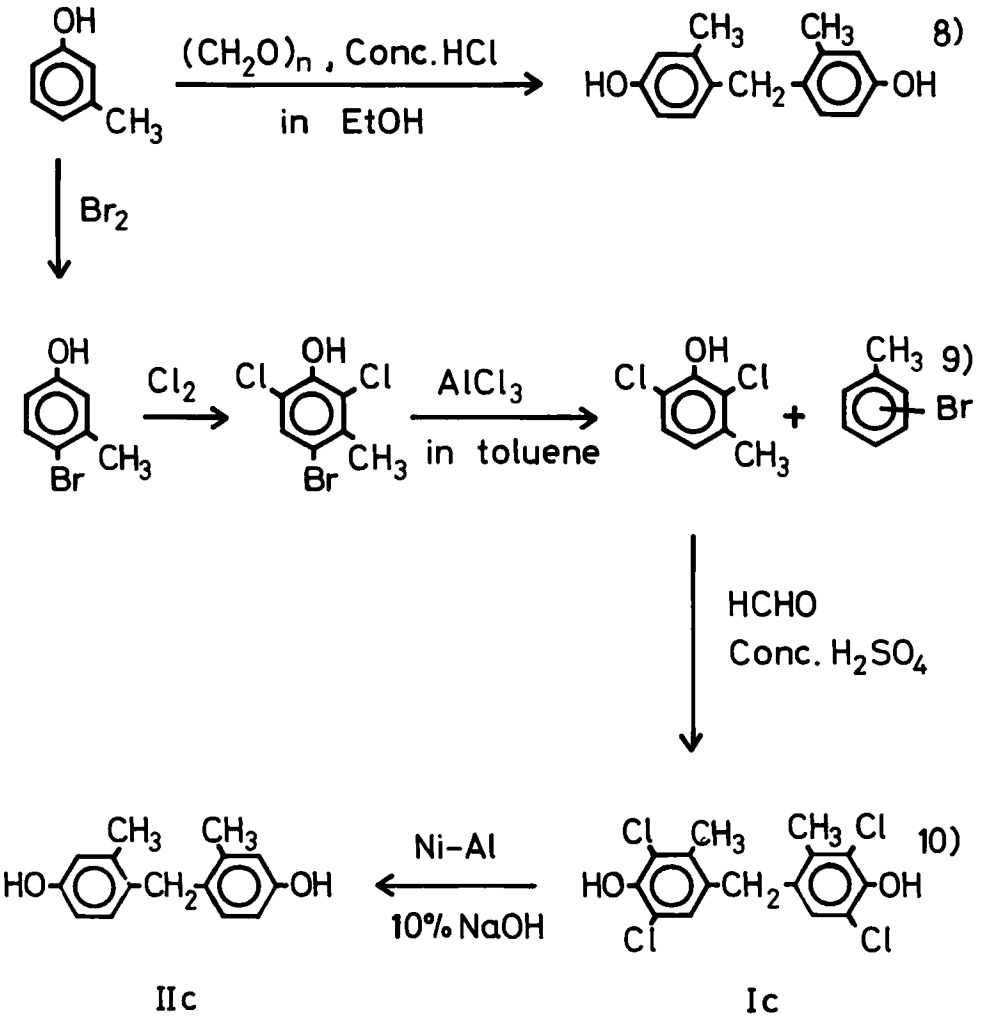
Table 1. The Reductive Dehalogenation of Halodihydroxydiphenylmethanes (I) in 10% NaOH Solution with Raney Ni-Al Alloy.

Run	I	Time(min)	Temp.(°C)	Product, II (%)	Mp.(°C)(lit.mp.)
1	a	20	rt.	a(95.5)	160-161(160-161)[7]
2	b	60	95-96	b(96)	128-130(127)[8]
3	c	60	95-96	c(93)	169-170(113)[8]

As is shown in Table 1, the expected products, 4,4'-dihydroxy- (II a), 4,4'-dihydroxy-3,3'-dimethyl- (II b) and 4,4'-dihydroxy-2,2'-dimethyldiphenylmethane (II c) were obtained in good yield. The structures of II were confirmed by comparison with the reported melting points[7-8] and their spectral and analytical data. Although the reported melting point of II c was 113° as shown in Table 1, II c obtained in this reaction

melted sharply at 169-170°. However, the spectral data and the course of our reaction strongly support the structure proposed by us for II c.

Therefore, Harden and Reid[8] might have obtained a different isomer of II c or a mixture of some isomers which could be formed in the reaction.



IIc Ic

Previously, II a and II b had usually been isolated from the novolacs which were obtained from phenol and o-cresol with formaldehyde in the presence of acidic catalyst. Our results recommend this reaction as more convenient preparation of these compounds.

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

Materials.- The halodihydroxydiphenylmethanes, 3,3',5,5'-tetrabromo- (Ia), 3,3'-dichloro-2,2'-dimethyl-4,4'-dihydroxydiphenylmethane (Ic) were previously prepared;[10]
Ia: mp. 224-226°(d). Ib: mp. 158-160°. Ic: mp. 166-167°.

4,4'-Dihydroxydiphenylmethane (II a).- To a solution of 10 g (19.4 mmole) of Ia in 200 ml of 10% sodium hydroxide was gradually added 10 g of Raney Ni-Al alloy in the period of 20 min, and then the insoluble substance was filtrated off. The filtrate was acidified with 10% hydrochloric acid, and 3.7 g (95%) of II a was precipitated as colorless needles, mp. 160-161°, lit.[7] mp. 160-161°.

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04.
Found: C, 77.85; H, 6.11.

IR cm^{-1}: 3300 (νOH). NMR (DMSO-d_6) δ ppm: 3.65 (s, 2H, CH_2), 6.65 (d, 4H, Jab = 9 cps, aromatic protons), 6.95 (d, 4H, Jab = 9 cps, aromatic protons) and 9.19 (broad s, 2H, OH).

4,4'-Dihydroxy-3,3'-dimethyldiphenylmethane (IIb).- To a solution of 2.97 g (10 mmole) of Ib in 80 ml of 10% sodium hydroxide was gradually added 3 g of Raney Ni-Al alloy. After addition of the alloy, the reaction mixture was warmed on a water bath (at 95-96°) for 1 hr and worked up as describe above to yield 2.2 g (96%) of IIb, mp. 128-130°, lit.[8] mp. 127°, as colorless prisms (from $CHCl_3$).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06.
Found: C, 78.65; H, 7.08.

IR cm^{-1}: 3300 (νOH). NMR spectrum of IIb could not measured since a suitable solvent could not be found.

4,4'-Dihydroxy-2,2'-dimethyldipphenylmethane (IIc).- Similarly a solution of 1 g (2.73 mmole) of Ic in 10 ml of 10% sodium hydroxide was treated with 2 g of Raney Ni-Al alloy and worked up as described above affording 0.58 g (93%) of IIc, mp. 169-170°, lit.[8] mp. 113°, colorless needles (from petroleum ether).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06.
Found: C, 78.97; H, 7.03.

IR cm^{-1}: 3200 (νOH). NMR (DMSO-d_6) δ ppm 2.11 (s, 6H, CH_3), 3.62 (s, 2H, CH_2), 6.35-6.80 (m, 6H, aromatic protons) and 9.01 (s, 2H, OH).

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