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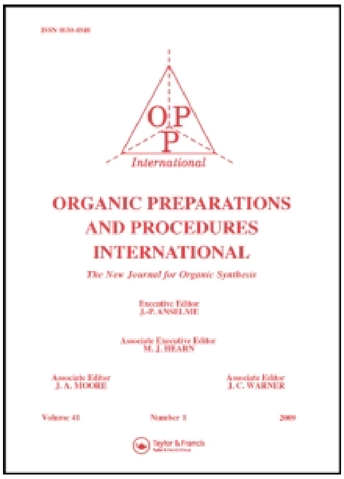

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Masashi Tashiro[a]; Gouki Fukata[a]
[a] Research Institute of Industrial Science, Kyushu University, Fukuoka, Japan

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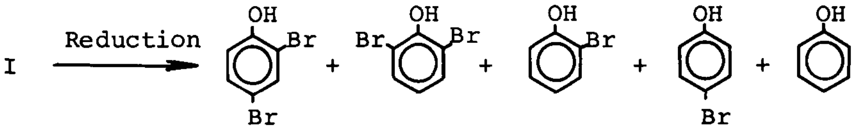
THE REDUCTIVE DEBROMINATION OF BROMOPHENOLS[1]

Masashi TASHIRO* and Gouki FUKATA
Research Institute of Industrial Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812, JAPAN

The report that treatment of 2,4,6-tribromophenol (I) with zinc powder in refluxing acetic acid gave 2,4-dibromophenol (II) as the sole product in 60% yield[2] prompted us to investigate the reductive debromination of I under various condition in order to find the method of selective preparation of desired halophenols by reductive dehalogenation of some halophenols. The reductive debromination I was carried out under various conditions (Table I). The possible products of the reduction of I are shown.



II III IV V VI

(1)

While Raney Ni-Al alloy[3] in 10% NaOH solution is the most powerful reducing agent, giving only phenol, zinc and aluminum powders are milder, affording II, III and IV at 20° (runs 2 and 5). However, tin is a weak and unselective agent giving the same amounts of II and III with a large quantity of recovered I. Other metals such as Fe, Ni, Co, Mg and Ti (powders) are inactive for the reaction of I in 10% NaOH solution at 80°.

IV was selectively formed in high yield when I was treated with zinc powder in 10% NaOH solution at 80°. The result seems to suggest that the reductive debromination method might be applicable to the preparation of *o*-bromophenol.

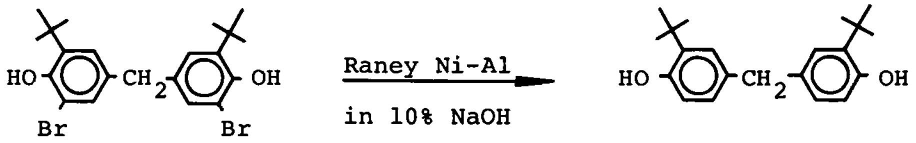
Table I. Reductive Debromination of I[a)]

Run	Metal[b)]	Solvent[c)]	Temp.(°C)	Time(hr)	Distribution of product (%)[d)]
1	Zn	B	80	1	IV(100)[e)]
2	Zn	B	20	2	II(27),III(56),IV(17)
3	Zn	A	reflux	2	II(100)[e)]
4	Ni-Al	B	20	2	VI(100)[e)]
5	Al	B	20	2	I(15),II(9),III(30), IV(34)
6	Sn	B	80	2	I(75),II(12),III(12)

a) I/Metallic powder : 0.1 g/0.2 g ; I/10% NaOH : 0.1 g/3 ml; I/10% HCl-EtOH : 0.1 g/0.5 ml-3 ml. b) The metallic powder such as Fe, Mg, Ti, Co and Ni were inactive for the reduction of I in 10% NaOH solution. c) A : 10%aq. HCl-EtOH, B : 10%aq. NaOH. d) Distribution of product was determined by gas chromatography. e) II, IV and VI were isolated in 97, 96 and 99% yields respectively.

In contrast to the basic medium, II was selectively obtained in higher yield than previously reported in 10% aqueous HCl-EtOH solution.[2] The preparations of II and IV using *t*-butyl as a positional protective group were previously reported.[3] However, the present reductive debromination of I seem to be more convenient than the previous method because the starting material for the preparation of the both II and IV is the same compound I which is easily obtained by bromination of VI.

The reductive debromination of 3,3'-dibromo-5,5'-di(t-butyl)-4,4'-dihydroxydiphenylmethane (VII), prepared by the acid-catalyzed reaction of 2-bromo-6-t-butylphenol with 38% formalin. With Raney Ni-Al alloy in 10% sodium hydroxide solution gave 3,3'-di-(t-butyl)-4,4'-dihydroxydiphenylmethane (VIII) in 62% yield, VIII was also obtained in low yield by the $AlCl_3$-CH_3NO_2 catalyzed transalkylation of 3,3',5,5'-tetra-(t-butyl)-4,4'-dihydroxydiphenylmethane (IX) carried out at -35° in toluene.



VII VIII

EXPERIMENTAL

All of the metallic powders such as zinc, Raney Ni-Al alloy, aluminum, magnesium, tin, titanium, cobalt, nickel and iron powder of commercial grade were used without purification. 2,4,6-Tribromophenol (I) was prepared according to the reported method and purified by recrystalization: mp 95-96°C; lit.[4], mp 96°C. The authentic samples of 2-bromo- (IV), 2,4-dibromo- (II) and 2,6-dibromophenol (III) were prepared as previously reported.[5] The analyses were carried out by gas chromatography using Yanaco YR-101, column 30% high silicon grease 75 cm; increasing rate of column temeprature, 12°/min. Carrier gas helium, 50 ml/min. From the area of individual peaks, mole% figure were calculated for each product.

General Procedure.- To a solution of 0.1 g (0.3 mmole) of I in 3 ml of 10% NaOH (or 3 ml of EtOH and 0.5 ml of 10% HCl), was gradually added 0.2 g of metallic powder at room temperature. After the mixture was stirred at a desired, constant temperature and a specified reaction time, the remained metallic powder was removed by filtration. The filtrate was acidified with 10% hydrochloric acid and extracted with benzene, and the benzene solution was dried over sodium sulfate and evaporated in vacuo to give the crude products which were analyzed.

Large Scale Procedure.

a) Preparation of IV.- To a solution of 25 g (77.6 mmoles) of I in 750 ml of 10% sodium hydroxide, was added gradually 50 g of zinc powder at room temperature. After the mixture was stirred at 80°C for 1 hr, the remained zinc powder was filtrated off, and the filtrate was acidified with 10% hydrochloric acid and extracted three times with 300 ml of benzene. The benzene solution was dried over sodium sulfate and evaporated in vacuo to afford 12.3 g (94%) of IV. The purity is higher than 99%.

b) Preparation of II.- To a solution of 10 g (30.2 mmoles) in 300 ml of ethanol and 50 ml of 10% hydrochloric acid, was gradually added 10 g of zinc powder. After the mixture was refluxed for 2 hr, the remained zinc powder was filtrated off, and the filtrate was evaporated in vacuo and extracted with 200 ml of benzene. The benzene solution was dried over sodium sulfate, and evaporated in vacuo to afford 7.4 g (97%) of II.

Preparation of 3,3'-Dibromo-5,5'-di(t-butyl)-4,4'-dihydroxydiphenylmethane (VII).- After a mixture of 1.0 g (4.4 mmole) of 2-bromo-6-t-butylphenol[6], 4 ml of 37% formalin and 3 ml of conc. sulfuric acid was warmed at 95° for 1 hr, the reaction mixture was poured into a large amount of water, and extracted with ether. The ethereal solution was dried over sodium sulfate and evaporated in vacuo to afford 0.44 g (43%) of VII which was recrystallized from petroleum ether (bp 30-60°) to give pale yellow prisms, mp 131.5-132.5°.

Anal. Calcd for $C_{21}H_{26}O_2Br_2$: C, 53.63; H, 5.57.

Found: C, 53.78; H, 5.60.

Ir cm^{-1}: 3540 (νOH). Nmr ($CDCl_3$) δ ppm: 1.36 (18H, s, $(C\underline{H}_3)_3$), 3.74 (2H, s, $C\underline{H}_2$), 5.67 (2H, s, $O\underline{H}$), 7.00 (2H, d, J = 2.25 Hz, aromatic protons) and 7.08 (2H, d, J = 2.25 Hz, aromatic protons).

Preparation of 3,3'-Di-(t-butyl)-4,4'-dihydroxydiphenylmethane (VIII).- To a solution of 80 mg (0.17 mmole) of VII in 2 ml of 10% sodium hydroxide was added 100 mg of Raney Ni-Al alloy at room temperature. After the reaction mixture was warmed at 95° for 15 min; the undisolved material was filtrated off. The filtrate was acidified with 10% hydrochloric acid, and extracted with ether. The extract was dried over sodium sulfate and evaporated *in vacuo* to afford 33 mg (62%) of VIII which was recrystallized from petroleum ether to give colorless prisms, mp 109.5-110.5°.

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

Found: C, 80.74; H, 9.10.

Ir cm^{-1}: 3500 (νOH). Mass spectrum m/e: 312 (M^+). Nmr ($CDCl_3$) δ ppm: 1.40 (18H, s, $(C\underline{H}_3)_3$), 3.82 (2H, s, $C\underline{H}_2$), 4.66 (2H, s, $O\underline{H}$), 6.45-7.20 (6H, m, aromatic protons).

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