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Aluminium-mediated Reductive Dimerization of Aromatic Dialdehydes†

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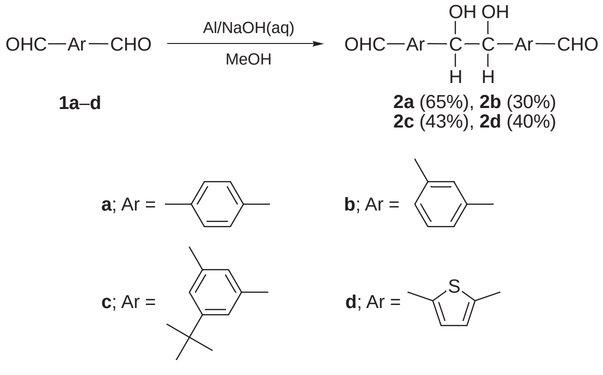
Pinacol coupling reaction of several aromatic dialdehydes **1a–d** using inexpensive aluminum powder as a reductive reagent in aqueous NaOH–methanol media afforded dimeric compounds **2a–d** as main products, in which only one carbonyl group of **1** was reduced.

Pinacol coupling reactions of aromatic aldehydes have been much used for the preparation of a wide range of vicinal diols.[1] It has been shown that inexpensive aluminium powder can be used as an effective reagent in the pinacol coupling reactions of aromatic aldehydes in aqueous media.[2] However, the coupling reactions of aromatic dicarbonyl compounds have been limited, until now, to the synthesis of macrocyclic compounds such as porphyrin derivatives[3] and cyclophane compounds.[4] There are also some reports concerning the polymerization of benzene-1,4-dicarbaldehyde to poly-(1,4-phenylene ethane-1,2-diol) by using Mukaiyama's reagent.[5]

When aromatic dialdehydes **1a–d** are treated with aluminium powder and an aqueous alkaline solution in methanol, 1,2-bis(formyl-substituted aryl)ethane-1,2-diols **2a–d** are formed as the main products in which only one carbonyl group of **1** is reduced, the other remaining unreacted. The diols **2a–d** are accompanied by minor amounts of polymerization products (Scheme 1). The ratios of (±)- and *meso*-isomers of **2a–d** were determined by ^{1}H NMR.[6] The coupling reactions of the 1,4-dialdehydes **1a** and **1d** showed a high (±)-selectivity. However, this was not the case for the 1,3-dialdehydes **1b**,**c**. One possible explanation for this difference can be the presence of the carbonyl group in the 4-position of the 1,4-dialdehydes. This carbonyl group can conjugate effectively with a radical centre to lower the reactivity of the intermediate formed in the coupling reaction. Thus, the sterically more favourable (±)-isomer may be preferred.[7]



Scheme 1

2,5-Dimethoxybenzene-1,4-dicarbaldehyde[8] is sparingly soluble in methanol and on treatment with aluminium powder, no coupling product could be obtained, nor could any starting material be recovered. Under identical conditions naphthalene-1,8-dicarbaldehyde, which exists in an equilibrium mixture with its hydrated form, also did not give the expected coupling products. Instead, the product of an intramolecular Cannizzaro reaction, 1,8-naphthalide,[9] was obtained in high yield (78%).

Only a few reports in the literature deal with specific reactions on only one carbonyl group of symmetric dialdehydes and these contain complicated experimental procedures or special reaction conditions.[10] On treatment with the Al/NaOH–MeOH reductive system, aromatic dialdehydes **1** gave the dimerization products **2**, which contain two hydroxy groups and two formyl functions in the molecule. Owing to their polyfunctionality, **2** could well find many applications as starting materials in further syntheses.

Experimental

Mps were determined on a Yanaco MP-500D Micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO IR 700 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX 270 (270 MHz) spectrometer using SiMe$_4$ as internal standard; *J* values are given in Hz. Mass spectra were recorded on a JEOL JMS-70 spectrometer. 3-Nitrobenzyl alcohol was used as a matrix for MS (FAB). Elemental analyses were determined on a Yanaco MT-S CHN Corder apparatus.

Commercially available aluminium powder (mesh 150, Kishida Chemical Co.) was used as received. Dialdehydes **1a–b** and **1d** are commercially available.

5-tert-*Butylbenzene*-1,3-*dicarbaldehyde* (**1c**).—Compound **1c** was prepared by a Sommelet reaction[8] as follows. A mixture of 3,5-bis(bromomethyl)-*tert*-butylbenzene[11] (3.2 g, 10 mmol), hexamethylenetetramine (3.0 g, 21.4 mmol), and aqueous 60% ethanol (40 ml) was heated under reflux for 20 h. After it had cooled, the mixture was extracted with dichloromethane. The organic layer was dried (MgSO$_4$) and the solvent was evaporated to afford the crude product which, on column chromatography using hexane–ethyl acetate (4:1), yielded **1c** (1.20 g, 63%) as colourless *plates* (from hexane), mp 63–64 °C; ν_{max}/cm^{-1} 2962, 2864, 2732; δ_H(CDCl$_3$) 1.42 (s, 9 H), 8.19 (s, 3 H), 10.12 (s, 2 H); δ_C 31.1, 35.2, 129.0, 131.6, 137.0, 153.7, 191.5; *m/z* (FAB) (%) 191 (M + H$^+$) (Found: C, 75.71; H, 7.47. C$_{12}$H$_{14}$O$_2$ requires C, 75.76; H, 7.42%).

General Procedure for Coupling Reaction of **1**.—To a mixture of **1** (5 mmol) and aluminium powder (0.45 g, 16.7 mmol) in methanol (15 ml), an aqueous 10% NaOH solution (6.7 ml) was added dropwise during 10 min at room temperature and under mechanical stirring. After the reaction mixture had been stirred at room temperature for 80 min, it was filtered and the filtrate was extracted with ethyl acetate. The extract was washed with water, dried (MgSO$_4$) and evap-

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orated *in vacuo* to afford a residue which was chromatographed on silica gel (Wako gel, C-300) using a mixture of hexane–ethyl acetate as an eluent, giving **2**.

1,2-*Bis*(4-*formylphenyl*)*ethane*-1,2-*diol* (**2a**) was eluted with hexane–ethyl acetate (1:1) as a 4:1-mixture of (±) and *meso*-isomers: colourless prisms (from AcOEt), mp 184–187 °C; ν_{max}/cm^{-1} 3446, 2842, 1686, 1424; δ_H of (±) isomer (DMSO-d_6) 4.81 (s, 2 H), 5.70 (s, 2 H), 7.35 (d, 2 H, *J* 8.3), 7.73 (d, 2 H, *J* 8.3), 9.93 (s, 2 H); δ_H of *meso*-isomer (DMSO-d_6) 4.71 (s, 2 H), 5.61 (s, 2 H), 7.46 (d, 2 H, *J* 7.9), 7.80 (d, 2 H, *J* 7.9), 9.97 (s, 2 H); *m/z* (FAB) (%) 271 ($M + H^+$, 8) (Found: C, 70.84; H, 5.32. $C_{16}H_{14}O_4$ requires C, 71.10; H, 5.22%).

1,2-*Bis*(3-*formylphenyl*)*ethane*-1,2-*diol* (**2b**) was eluted with hexane–ethyl acetate (1:1) as a 4:3-mixture of (±) and *meso*-isomers: colourless oil; ν_{max}/cm^{-1} 3446, 2842, 1686; 1424; δ_H of (±) isomer (DMSO-d_6) 4.83 (s, 2 H), 5.65 (s, 2 H), 7.41–7.83 (m, 8 H), 9.92 (s, 2 H); δ_H of *meso*-isomer (DMSO-d_6) 4.69 (s, 2 H), 5.56 (s, 2 H), 7.83–7.41 (m, 8 H), 9.99 (s, 2 H); *m/z* (FAB) (%) 271 ($M + H^+$, 8) (Found: C, 70.61; H, 5.40. $C_{16}H_{14}O_4 \cdot \frac{1}{6} H_2O$ requires C, 70.32; H, 5.29%).

1,2-*Bis*(5-tert-*butyl*-3-*formylphenyl*)*ethane*-1,2-*diol* (**2c**) was eluted with hexane–ethyl acetate (4:1) as a 3:2-mixture of (±) and *meso*-isomers; colourless solid, mp 57–60 °C; ν_{max}/cm^{-1} 3446, 2962, 1698; δ_H of (±)-isomer ($CDCl_3$) 1.19 (s, 18 H), 3.10 (s, 2 H), 4.78 (s, 2 H), 7.19–7.78 (m, 6 H), 9.92 (s, 2 H); δ_H of *meso*-isomer ($CDCl_3$) 1.22 (s, 18 H), 2.68 (s, 2 H), 5.06 (s, 2 H), 7.19–7.78 (m, 6 H), 9.93 (s, 2 H); *m/z* (%) 382 (M^+, 1), 191 ($M^+/2$, 32) (Found: C, 74.76; H, 7.94. $C_{24}H_{30}O_4 \cdot 1/4H_2O$ requires C, 74.49; H, 7.94%).

1,2-*Bis*(5-*formylthiophen*-2-*yl*)*ethane*-1,2-*diol* (**2d**) was eluted with hexane–ethyl acetate (1:1) as a 5:1-mixture of (±) and *meso*-isomers: colourless solid mp 107–130 °C; ν_{max}/cm^{-1} 3422, 1662; δ_H of (±)-isomer (DMSO-d_6) 5.09 (s, 2 H), 6.43 (s, 2 H), 7.08 (d, 2 H, *J* 4.0), 7.80 (d, 2 H, *J* 4.0), 9.79 (s, 2 H); δ_H of *meso*-isomer (DMSO-d_6) 4.96 (s, 2 H), 6.39 (s, 2 H), 7.14 (d, 2 H, *J* 3.6), 7.84 (d, 2 H, *J* 3.6), 9.83 (s, 2 H); *m/z* (FAB) (%) 283 ($M + H^+$, 15) (Found: C, 51.16; H, 3.68. $C_{12}H_{10}O_4S_2$ requires C, 51.05; H, 3.57%).

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