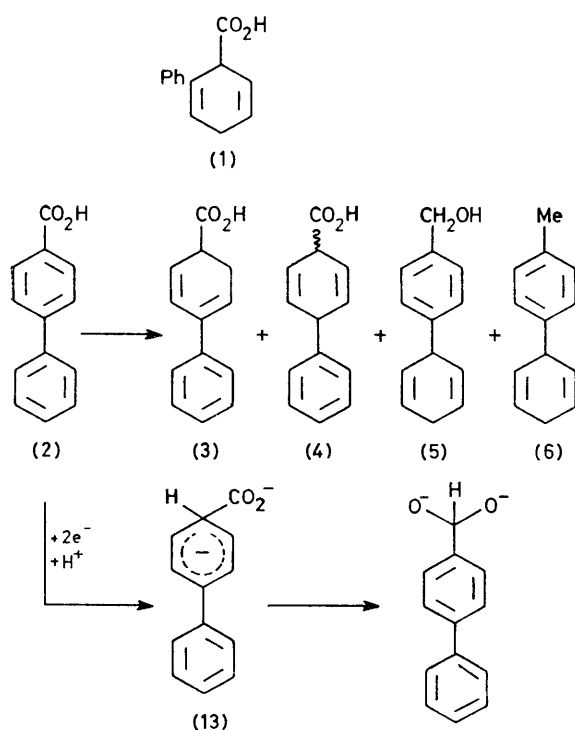


## Reduction of the Carboxyl-function in Aromatic Carboxylic Acids by Alkali Metal–Liquid Ammonia Solutions

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*Summary* Significant yields of alcohol and hydrocarbon products which are obtained in the reduction of 4-phenylbenzoic acids result from increased conjugation in the reaction intermediates.

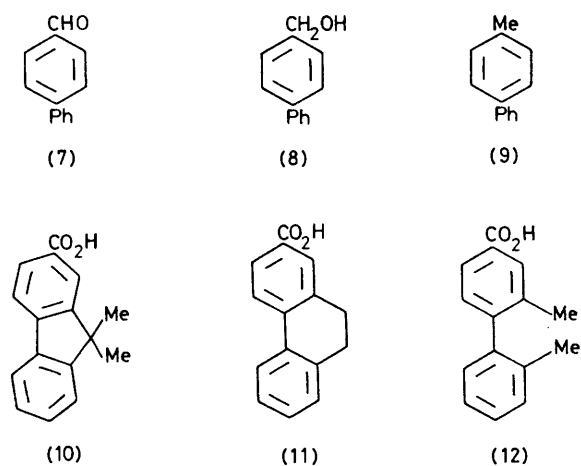
WHILST Birch reduction<sup>1-3</sup> of biphenyl-2-carboxylic acid (4 mol. equiv. Li or Na-NH<sub>3</sub>; NH<sub>4</sub>Cl *etc.*) leads to high yields of the 1,4-dihydrobenzoic acid (1) as the sole identifiable product, from similar treatment of biphenyl-4-carboxylic acid (2) there is obtained, in addition to the expected 1,2- and 1,4-dihydrobenzoic acids (3) and (4) respectively and recovered starting material, a 25% yield of a mixture of an alcohol and a hydrocarbon. These have been characterised as 1,4-dihydro-4'-hydroxymethylbiphenyl (5) and 1,4-dihydro-4'-methylbiphenyl (6) respectively by spectroscopic studies, and, in the latter case, by dehydrogenation (tetrachloro-*p*-benzoquinone) which affords 4-methylbiphenyl, identical with authentic material. In the presence of ethanol as a proton source, there are obtained from (2) over-reduced acids in addition to (4), but only traces of the alcohol (5) and hydrocarbon (6) are detected. This reduction of the carboxy-function under such conditions is, to our knowledge, without precedent.†



A careful re-examination of the reduction of benzoic acid (4 mol. equiv. Na-NH<sub>3</sub>; NH<sub>4</sub>Cl), however, reveals the presence of very small quantities of non-acidic material (4%) which we have identified (g.l.c.) as benzaldehyde, benzyl alcohol, and toluene and their dihydro derivatives. It thus seems that the most likely pathway for the conversion of 4-phenylbenzoic acid into the hydrocarbon (6) would proceed through 4-phenylbenzaldehyde (7) and

4-hydroxymethylbiphenyl (8) as intermediates. Indeed reduction of the aldehyde (7) leads to a mixture of the alcohol (8) (68%) together with reduced and unreduced hydrocarbons (6) and (9) respectively (28%).‡ Similarly from the alcohol (8) there is obtained 1,4-dihydro-4'-methylbiphenyl (6) (91%) as the only identifiable product.<sup>4</sup> When the acid (2) is reduced with a greater excess (10 mol. equiv.) of alkali metal there is obtained a higher proportion of non-acidic material (*ca.* 35%) which consists only of 1,4-dihydro-4'-methylbiphenyl (6).

One major difference between biphenyl-4-carboxylic acid (2) and other aromatic acids which we have studied lies in the ability of (2) to delocalise the excess electron density in its radical anion or dianion over two aromatic rings. Indeed Harvey and others have found<sup>5</sup> that whilst terminal ring-reduced product dominates in the reduction of *p*-terphenyl, with *o*-terphenyl only the middle ring is reduced. In this latter example, as in biphenyl-2-carboxylic acid (1), the aromatic rings cannot readily lie coplanar owing to steric interactions. In order to see whether such conjugation is the dominant factor in this process we have also studied the reduction of the biphenylcarboxylic acids (10—12) in which



the two benzene rings are tilted at varying degrees with respect to each other. Whilst reduction of the rigidly planar fluorenicarboxylic acid (10) or the slightly twisted dihydrophenanthroic acid (11) again leads to relatively high yields§ of the expected non-acidic products (in 19 and 17% yield respectively), a reduced proportion of non-acidic material (*ca.* 10% when 4 mol. equiv. of Li are used) is obtained from the *o*-bitolylcarboxylic acid (12). In this latter compound the two phenyl rings are prevented from lying coplanar by steric interaction of the *ortho*-substituents.

We believe that in these reductions partitioning between the different reaction pathways results from protonation at different sites in the initially formed radical-anion or dianion, in a manner similar to that observed in the reduction of *p*-terphenyl.<sup>5</sup> In particular, protonation of the

† The reduction of aliphatic carboxylic acids to aldehydes has been observed in Li-MeNH<sub>2</sub>, however (A. O. Bedenbaugh, J. H. Bedenbaugh, W. A. Bergin, and J. D. Adkins, *J. Amer. Chem. Soc.*, 1970, **92**, 5774).

‡ Under similar conditions benzaldehyde affords benzyl alcohol and a little toluene. This reaction does not appear to have been examined in detail previously (refs. 1 and 2 and C. A. Kraus and G. F. White, *J. Amer. Chem. Soc.*, 1923, **45**, 770).

§ The reduced yield of non-acidic material from (10) when compared with (2) may reflect a methyl substituent effect on the stability of, or charge distribution in, the reaction intermediates.

carbon atom bearing the carboxylate group may be favoured by the enhanced stability of the resulting intermediate (**13**) through conjugation of the cyclohexadienyl radical, or anion, with the phenyl substituent. A hydride shift on to the carboxy-carbon atom could then lead to reduction of this substituent. We are currently attempting to obtain evidence for such a reaction pathway.

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<sup>1</sup> G. W. Watt, *Chem. Rev.*, 1950, **46**, 317.

<sup>2</sup> A. J. Birch and G. Subba Rao, *Adv. Org. Chem.*, 1972, **8**, 1.

<sup>3</sup> R. G. Harvey, *Synthesis*, 1970, 161.

<sup>4</sup> The Birch reduction of other biphenyl derivatives has been described, *e.g.* D. F. Lindlow, C. N. Cortez, and R. G. Harvey, *J. Amer. Chem. Soc.*, 1972, **94**, 5406; A. J. Birch and G. Nadamuni, *J.C.S. Perkin I*, 1974, 545.

<sup>5</sup> R. G. Harvey, D. F. Lindlow, and P. W. Rabideau, *J. Amer. Chem. Soc.*, 1972, **94**, 5412.