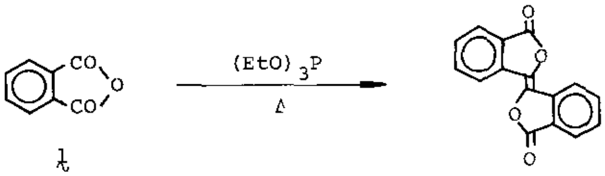
A ONE POT REACTION INVOLVING HYDROLYSIS-REDUCTION OF BIPHTHALYLIDENE IN AN ALKALINE MEDIUM

Masashi Tashiro*, Tsuyoshi Sumida and Gouki Fukata
Research Institute of Industrial Science, Kyushu University 86,
Hakozaki, Higashi-ku, Fukuoka 812, JAPAN

Abstract —— The hydrolysis of biphthalylidene (**2**) in a varying alkaline medium afforded selectively 2,2'-dicarboxybenzoin (**3**) or 5,5'-dihydro-5-oxo-diphthalylidene (**4**) in good yields depending upon the conditions used. In one pot reaction involving hydrolysis of **2** followed by reduction with Raney-alloys, 4b,10b-dihydrobenzopyrano[4,3-c]benzopyrano-6,12-dione (**9**) was almost selectively obtained in good yields. In the case of the combination of hydrolysis in 10% KOH aq and Al-Ni alloy reduction, 2,2'-dicarboxybibenzyl (**8**) yielded in 51% as a sole product.

Although biphthalylidene (**2**) has been prepared by a reduction of phthalic anhydride (**1**) with triethyl phosphite[1] and **2** seems to be a good starting material for organic synthesis, its reactivity is slightly known by today.



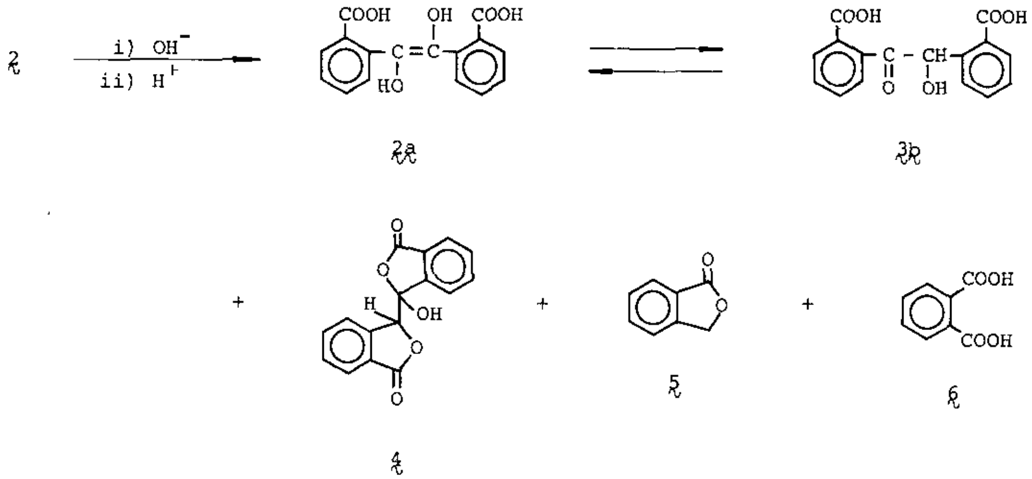
1

2

We wish to report on a one pot reaction involving hydrolysis and reduction with Raney-alloys of **2** in an alkaline medium.

First, the hydrolysis of **2** was carried out under various conditions and the results are summarized in Table 1.

Under the mild conditions, the dicarboxylic acid (**3**) [colorless needles (DMSO-H_2O), 281-283°] was obtained in 62% yield (Run 5). This product **3** seems to be a mixture of two tautomeric isomers, **3a** and **3b**, however, their distribution can not



2a 3b 4 5 6

Table 1. Hydrolysis of Biphthalylidene (2)

Run	Conditions	Product (%)$^{a)}$
1	NaOEt-EtOH, reflux for 10 min	4 (26)
2	10% KOH aq, reflux for 2 h	4 (69)
3	10% KOH aq, reflux for 15 h	4 (45), 5 (27), 6 (27)
4	5% KOH-EtOH, reflux for 2h	4 (96)
5	5% KOH aq, room temp. for 72 h	3 (62)

a) The yields isolated are shown.

be determined by the available data.$^{2)}$ As are shown in Runs 1-4, the compound 4$^{3)}$ [colorless needles, mp. 220° (d.)] was formed under the more drastic conditions in the respective cases. It was also found that phthalide (5) and phthalic acid (6) besides 4 were obtained.

A one pot reaction involving the hydrolysis and the reduction with such Raney-alloys of 2 in an alkaline medium was carried out in order to obtain 2,2'-dicarboxylbibenzyl which is a key compound for the preparation of macro cyclic compounds and the results are summarized in Table 2. The kind of the products depends upon the conditions used. The combination of hydrolysis condition A and Ni-Al alloy reduction afforded o-toluic acid (7) and the compound (9) [white amorphous (EtOH), mp. 282-288° (d.)], respectively (Run 1-2). The former 7 might be produced by the reduction of 5 which is one of products of the hydrolysis of 2. The later compound 9 might be assumed as 4b,10b-dihydrobenzopyrano[4,3-c]benzo-

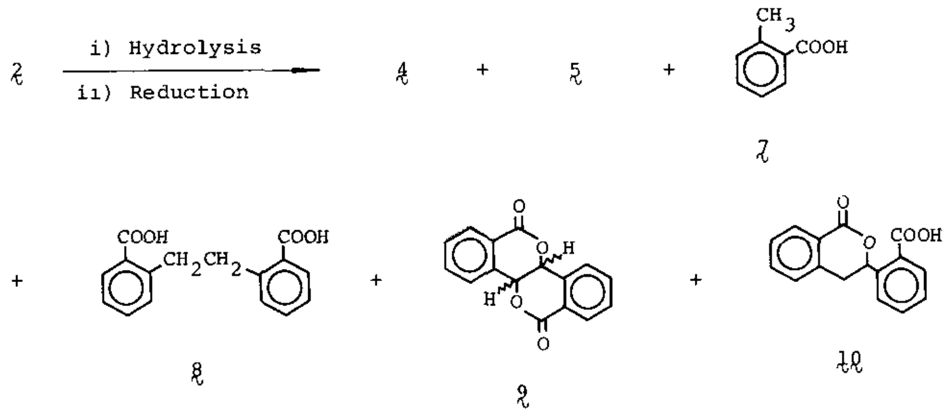


Table 2. A One Pot Reaction Involving Hydrolysis and Reduction of 2

Run	Conditions Hydrolysis[a]	 Reduction	Product (%)[b]
1	A	Ni-Al, reflux for 3 h	7 (33), 9 (52)
2	A	Ni-Al, room temp. for 6 h	7 (35), 9 (32)
3	A	Cu-Al, reflux for 3 h	5 (35), 9 (29)
4	A	Fe-Al, reflux for 3 h	4 (32), 5 (32)
5	B	Ni-Al, reflux for 3 h	8 (51), 9 (trace)
6	B	Cu-Al, reflux for 3 h	8 (trace), 9 (77)
7	C	Ni-Al, reflux for 3 h	9 (85), 10 (trace)

a) A: 10% KOH aq, reflux for 15 h; B: 10% KOH aq, reflux for 2 h; C: 10% NaOH aq/EtOH, reflux for 2 h.

b) The yields isolated are shown.

pyrano-6,12-dione by its spectral data[4] as well as elemental analysis, however, its steric structure is still not clear. In the case of hydrolysis condition C and the reduction with Ni-Al alloy (Run 7), the compound 10 [colorless needles (CH_3CN-H_2O), mp. 206-207°] was formed in only poor yield together with main product (9). This minor product 10 might be assumed as 3-(2-carboxyphenyl)3,4-dihydro-isocoumarin.[5] Based on the data of Run 1-4, the reducing activity of Raney-alloys is in the following order; Ni-Al>Cu-Al>Fe-Al. The same order was observed in the reduction of halophenols.[6]

The selective reductive products such as 8 and 9 were obtained in the cases of Run 5-7. From the above results, this one pot reaction; hydrolysis-reduction seems to be a method for the preparation of **8** and **9**.

REFERENCES AND NOTES

1. F. Ramirez, H. Yamanaka and O. H. Basedow, *J. Am. Chem. Soc.*, **83**, 173 (1961).
2. IR (KBr): ν_{OH} = 3250 cm^{-1}, ν_{CO} = 1740 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 7.30-8.06 (m, 8H, aromatic protons), 7.70 (s, 1H; disappeared with D_2O), 8.50 (s, 2H; disappeared with D_2O), 8.70 ppm (s, 1H; disappeared with D_2O). M.S.: m/e = 300 (M^+).
3. a) M. P. Cava, D. R. Napier and R. J. Pohl, *J. Am. Chem. Soc.*, **85**, 2076 (1963).
   b) C. Graebe and H. Schmalzigaug, Ann., **228**, 134 (1885).
4. IR (KBr): ν_{CO} = 1760 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 6.40 (s, 2H), 7.03-7.20 (m, 2H, aromatic protons), 7.60-8.00 ppm (m, 6H, aromatic protons). M.S.: m/e = 266 (M^+).
5. IR (KBr): ν_{OH} = 2945 cm^{-1}, ν_{CO} = 1750, 1685 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ = 3.31 (dd, 1H, *J* 9 and 13.5 Hz), 3.91 (dd, 1H, *J* 3 and 13.5 Hz), 5.87 (dd, 1H, *J* 3 and 9 Hz), 7.50 (s, 1H; disappeared with D_2O), 7.20-8.10 pp, (m, 8H, aromatic protons). M.S.: m/e = 268 (M^+).
6. a) M. Tashiro, A. Iwasaki and G. Fukata, "The Reports of Research Institute of Industrial Science", No. 65, Kyushu University, 1977, p.19.
   b) M. Tashiro, A. Iwasaki and G. Fukata, *J. Org. Chem.*, **43**, 196 (1978).

Received, 26th February, 1980