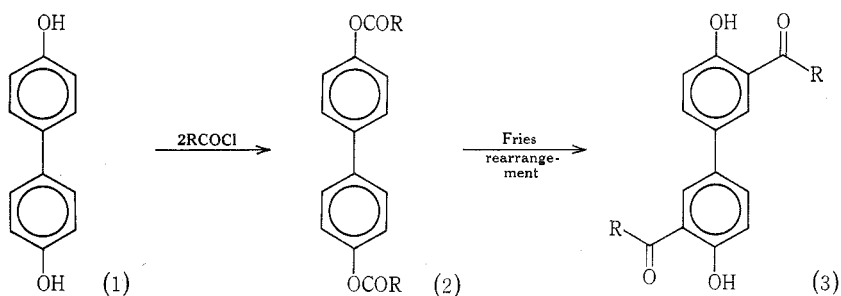


# SYNTHESIS OF 3,3'-DIACYL-4,4'-DIHYDROXYBIPHENYL

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Bis-*ortho*-hydroxy ketones of the type (3), which are finding increasing use as antioxidants, ultraviolet absorbers, bidentate ligands, intermediates to semiconductors and thermostable polymers,<sup>1-3</sup> have been made by Fries rearrangement of biphenyl esters (2).<sup>4-6</sup> The preparation of the esters hitherto has been unsatisfactory, mainly for solubility reasons,<sup>6</sup> and reported procedures for Fries rearrangement are unsuitable for large-scale preparations. We now report satisfactory experimental procedures.



- |                  |                      |
|------------------|----------------------|
| (a) R = methyl   | (g) R = n-heptyl     |
| (b) R = ethyl    | (h) R = n-nonyl      |
| (c) R = n-propyl | (i) R = n-undecyl    |
| (d) R = isobutyl | (j) R = n-tridecyl   |
| (e) R = n-pentyl | (k) R = n-pentadecyl |
| (f) R = n-hexyl  | (l) R = phenyl       |

Good yields of the esters (2) can be obtained by using dioxan as solvent instead of chlorobenzene,<sup>6</sup> reducing reaction time, and simplifying the work-up by pouring

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<sup>5</sup> Boon Long, N. J., *Pharm. Ass. Siam*, 1948, **1**, 5 (*Chem. Abstr.*, 1949, **43**, 5017).

<sup>6</sup> Pakkal, R., Thomas, F. D., and Fernelius, W. C., *J. chem. Soc.*, 1960, **25**, 282.

the reaction mixture into water. The yields of esters are consistently higher than those reported,<sup>6</sup> particularly for (2f) (52% instead of 22%). The results are summarized in Table 1.

TABLE 1  
COMPARATIVE YIELDS  
Yields in parentheses are from ref. 6

Diester	Yield (%)	Ketone	Yield (%)	Diester	Yield (%)	Ketone	Yield (%)
(2a)	93 <sup>a</sup> (62)	(3a)	70 <sup>b</sup> (19)	(2g)	84 (63)	(3g)	
(2b)	84 (77)	(3b)	97 <sup>b</sup> (58)	(2h)	70 <sup>d</sup>	(3h)	75 <sup>d,e</sup>
(2c)	75 (63)	(3c)	93 <sup>b</sup> (89)	(2i)	75 (70)	(3i)	(85)
(2d)	60 <sup>c</sup>	(3d)	99 <sup>b,c</sup>	(2j)	75 <sup>f</sup>	(3j)	72 <sup>e,f</sup>
(2e)	75 (73)	(3e)	99 <sup>b</sup> (53.3)	(2k)	79 <sup>g</sup>	(3k)	76 <sup>e,g</sup>
(2f)	52 (22)	(3f)	85 <sup>b</sup> (52.4)	(2l)	80 (77)	(3l)	51 (30)

<sup>a</sup> For acylation acetic anhydride was used. <sup>b</sup> Catalyst was  $\text{AlCl}_3\text{--NaCl}$  melt. <sup>c</sup> For the diester: m.p. 130° (Found: C, 74.4; H, 7.4). For the ketone: m.p. 94–95° (Found: C, 74.4; H, 7.4.  $\text{C}_{22}\text{H}_{26}\text{O}_4$  requires C, 74.6; H, 7.4%). <sup>d</sup> For the diester: m.p. 112–113° (Found: C, 77.7; H, 9.4). For the ketone: m.p. 74–75° (Found: C, 77.7; H, 9.4.  $\text{C}_{32}\text{H}_{46}\text{O}_4$  requires C, 77.7; H, 9.4%). <sup>e</sup> Prepared according to ref. 6. <sup>f</sup> For the diester: m.p. 114–115° (Found: C, 79.2; H, 10.3). For the ketone: m.p. 87–88° (Found: C, 78.9; H, 10.4.  $\text{C}_{46}\text{H}_{62}\text{O}_4$  requires C, 79.2; H, 10.3%). <sup>g</sup> For the diester: m.p. 110–112° (Found: C, 79.7; H, 10.1). For the ketone: m.p. 90–91° (Found: C, 79.7; H, 10.4.  $\text{C}_{44}\text{H}_{70}\text{O}_4$  requires C, 79.7; H, 10.6%).

The rearranged bis-*ortho*-hydroxy ketones (3a–f) and (3l) are obtained in excellent yield by using aluminium chloride–sodium chloride melt (molar ratio 7.5 : 3.43, m.p. 140°).<sup>7,8</sup> The reaction is carried out by adding the ester to the melt, rapidly increasing the temperature to 200° and maintaining it there for 2 min before quick cooling. Unlike the reported method,<sup>6</sup> in which monoketonic product is also obtained (as confirmed by t.l.c. and dry column chromatography<sup>9</sup>), the melt technique gives only the fully rearranged Fries product. Table 2 gives comparative yields obtained with various combinations of molten salts; the best results were given by aluminium chloride–zinc chloride in the molar ratio of about 5.1 : 1.

TABLE 2  
YIELDS (%) OF PRODUCTS (3a) AND (3l) WITH DIFFERENT CATALYST COMPOSITIONS  
For  $\text{AlCl}_3$  alone, reaction was at  $130 \pm 3^\circ$  for 24 hr; all others at 140–200° for 2 min

Starting material	$\text{AlCl}_3$ (3 g)	$\text{AlCl}_3\text{--NaCl}$ (10 g/2 g)	$\text{AlCl}_3\text{--ZnCl}_2$ (10 g/2 g)	$\text{AlCl}_3\text{--ZnCl}_2$ (6.6 g/2 g)	$\text{AlCl}_3\text{--ZnCl}_2$ (6.6 g/2.4 g)
Diester (2a), 7.4 mmol	40	70	82	38	13
Diester (2l), 5.0 mmol	—	51	57	34	—

Molten salt rearrangement is not applicable for esters beyond seven carbon atoms in the acyl moiety of (2) due to extensive decomposition around 200°. At lower

<sup>7</sup> Bruce, D. B., Sorrie, A. J. S., and Thomson, R. H., *J. chem. Soc.*, 1953, 2403.

<sup>8</sup> Gordon, J. E., in "Techniques and Methods of Organic and Organometallic Chemistry." (Ed. D. B. Denney.) Vol. I, p. 51. (Marcel Dekker: New York 1969.)

<sup>9</sup> Loev, B., and Goodman, M. M., *Chem. Ind.*, 1967, 2026.

temperature (140°) no rearrangement occurs. Esters (2h), (2j), and (2k) have been rearranged in 72–75% yields by the method reported previously.<sup>6</sup>

### Experimental

#### *4,4'-Dipropionyloxybiphenyl (2b)*

To a solution of the phenol (1) (18.6 g, 0.1 mol) in dioxan (100 ml), propionyl chloride (23 g 0.25 mol) was added slowly under anhydrous conditions. The mixture was refluxed for 4 hr, cooled, and poured into cold water. It was filtered, washed with water (4 × 50 ml), and dried to give 25 g (84%) of the ester (2b). This general procedure was used for preparing esters (2c–l) listed in Table 1.

#### *3,3'-Dipropionyl-4,4'-dihydroxybiphenyl (3b)*

To a melt of sodium chloride (2 g, 34.2 mmol) and aluminium chloride (10 g, 75 mmol) was added the ester (2b) (2 g, 6.7 mmol) at 140°. The temperature of the melt was raised rapidly to 200° and maintained there for 2 min. The reaction mixture was cooled and decomposed with hydrochloric acid (4*N*, 20 ml). The precipitate was filtered, washed, dried, and recrystallized from ethanol giving the hydroxy ketone (3b), 1.94 g (97%), m.p. 143–144°. This general procedure was used for preparing the bis-*o*-hydroxy ketones (3e–f) listed in Table 1.

#### *3,3'-Didecanoyl-4,4'-dihydroxybiphenyl (3h) and 3-Decanoyl-4,4'-dihydroxybiphenyl*

The pulverized ester (2h) (51.4 g, 0.1 mol) and aluminium chloride (33 g, 0.247 mol) were mixed in chlorobenzene (500 ml) and refluxed for 24 hr. After cooling, the reaction mixture was decomposed with hydrochloric acid (4*N*, 500 ml). Chlorobenzene was removed by steam distillation and the solid residue was filtered under suction, washed, and dried to give a solid A (48.8 g) shown to be a mixture of double and mono Fries rearrangement products by thin-layer chromatography on silica gel. Recrystallization of solid A (1 g) from dioxan–alcohol (1 : 1) afforded light yellow crystalline plates of (3h) (0.75 g, 71%), m.p. 74–75°.

Chromatography grade silica gel (100 g) was deactivated by adding water (15 ml) and packed in a glass column (53 by 3 cm). The crude product A (1 g) was dissolved in ether (10 ml), mixed with silica gel (5 g), and the solvent evaporated off. The dried product adsorbed on silica gel was transferred to the column and covered with glass beads. The column was developed with light petroleum (b.p. 60–80°)–butyl ether (80 : 20) under suction (120–180 mm). The solvent front was allowed to reach the bottom of the column and the zone,  $R_F$  0.38, was cut out, extracted with ether, and the solvent removed leaving a solid. Recrystallization from ethanol gave 0.2 g (19%) of 3-decanoyl-4,4'-dihydroxybiphenyl, m.p. 90–91° (Found: C, 78.2; H, 8.7. Calc. for  $C_{22}H_{28}O_2$ , C, 77.6; H, 8.2%).