1-Methoxymethyl-6,7-dimethoxy-3,4-dihydroisoquinoline (IV). A mixture containing 15 g. of *N*-homoveratrylmethoxyacetamide[4] (III), 150 ml. of dry toluene and 30 ml. of phosphorus oxychloride was refluxed and worked up as in the preparation of I. The product, 6 g. (43%), was isolated by distillation, b.p. 150–160° (0.7 mm.). The analytical sample boiled at 149° (0.7 mm.).

Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.30; H, 7.24; N, 5.96. Found: C, 65.96; H, 7.29; N, 5.97.

1-Methoxymethyl-6,7-dimethoxyisoquinoline (II). (a) *By action of methanolic potassium hydroxide on* I. A 1-g. sample of the dichloromethylisoquinoline (I) was refluxed with 10 ml. of 5% methanolic potassium hydroxide solution for 1 hr. (steam bath). The dichloro compound (I) dissolved, and precipitation of potassium chloride was soon observed. At the end of the hour the weight of the inorganic salt corresponded closely with that expected if 2 mol. equivalents of potassium chloride had formed. The filtrate was diluted with water and extracted repeatedly with benzene. The solution was treated with Norit, dried, concentrated and diluted with petroleum ether. The product which separated in 80–94% yield melted at 110–120°, and showed a negative test for halide. Recrystallized from ligroin it melted at 122.5–123.5°. A solution of the product in dilute hydrochloric acid gave a bright yellow fluorescence.

(b) *By dehydrogenation of 1-methoxymethyl-6,7-dimethoxy-3,4-dihydroisoquinoline* (IV). Dehydrogenation of the dihydroisoquinoline IV with 10% palladium charcoal catalyst was effected by heating at 160–175°. The product, b.p. 160–165° (1 mm.), obtained in 60% yield, solidified and on crystallization from ligroin, had m.p. 122–123°. This material did not depress the melting point of the product obtained by Procedure (a).

Anal. Calcd. for $C_{13}H_{15}NO_3$: C, 66.95; H, 6.44; N, 6.02. Found: C, 67.30; H, 6.52; N, 6.39.

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[4] This material, m.p. 40–43°, was prepared by the reaction of methoxyacetyl chloride [R. Leimu, *Ber.*, **70**, 1040 (1937)] with homoveratrylamine.

Study of the Double Fries Rearrangement. II. Rearrangement of Diesters of 4,4'-Biphenol

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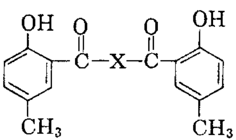
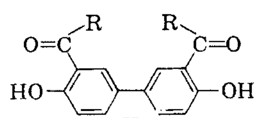
The preparation of a series of bis(*o*-hydroxyketones) of type I where X represents $(CH_2)n$ or *m*- or *p*-phenylene has been reported.[2]



I



II

A similar series of type II where the bis-functional starting material was a biphenol rather than a dicarboxylic acid was also desired. Although there has been a moderate amount of work on the Fries rearrangement of esters of polyhydroxybenzenes,[3] only two studies report the rearrangement of diesters of 4,4'-biphenol[4] to give 3,3'-diacetyl-4,4'-biphenol[4a,b] and 3,3'-dipropanoyl-4,4'-biphenol,[4a] whereas attempts to prepare 3,3'-dilauroyl-4,4'-biphenol were unsuccessful.[4b]

In the present study a number of esters of 4,4'-biphenol was prepared by treating the phenol with a series of acid halides in chlorobenzene solution. Each of these esters, when subjected to the Fries rearrangement under conditions previously described,[2] gave the corresponding 3,3'-diacyl-4,4'-biphenols in yields ranging from 19 to 92%.

Infrared spectra. The infrared spectra of the bis(*o*-hydroxyketones) show no absorption in the region of 2.77–2.79 μ (3610–3584 cm.$^{-1}$) characteristic of the free phenolic hydroxyl group, but they do exhibit one rather sharp absorption band in the region of 3.32–3.46 μ (3012–2890 cm.$^{-1}$). This corresponds to the broad absorption bands extending from 2.8–3.6 μ (3571–2778 cm.$^{-1}$) reported by Martin[5] for salicylaldehyde and *o*-hydroxyacetophenone which were attributed to the absorption of the hydroxyl group hydrogen bonded to the carbonyl group and, in part, to the carbon-hydrogen stretching frequency. Gordy[6] noted that the characteristic carbonyl group absorption of acetophenone at 5.96 μ (1678 cm.$^{-1}$) was shifted, in the case of *o*-hydroxyacetophenone, to 6.17 μ (1621 cm.$^{-1}$), due probably, to hydrogen bonding with the *o*-hydroxyl group. In a similar manner, each of the bis(*o*-hydroxyketones) exhibited one sharp absorption peak in the 6.10–6.14 μ (1639–1629 cm.$^{-1}$) region which could also be attributed to the absorption of the carbonyl group hydrogen-bonded to the *o*-hydroxyl group.

EXPERIMENTAL[7]

A. *4,4'-Biphenol esters.* All of the esters of 4,4'-biphenol were prepared from the same molar proportions and in the same general way as described for 4,4'-biphenol diacetate. Pertinent information is assembled in Table I.

4,4'-Biphenol diacetate. A solution of acetyl chloride (8.6 g., 0.11 mol.) in 25 ml. of dry chlorobenzene was added dropwise to a solution of 4,4'-biphenol (9.3 g., 0.05 mol.) and 25

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[1] Appointment supported by the International Cooperation Administration under the Visiting Research Scientists Program administered by the National Academy of Sciences of the United States of America.

[2] F. D. Thomas II, M. Shamma, and W. Conard Fernelius, *J. Am. Chem. Soc.*, **80**, 5864 (1958).

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[4] (a) R. W. Stoughton, R. Baltzly, and A. Bass, *J. Am. Chem. Soc.*, **56**, 2007 (1934). (b) N. Boon-Long, *J. Pharm. Assoc. Siam*, **1**, No. 4, 5 (1948). [*Chem. Abstr.*, **43**, 5017h (1949)].

[5] A. E. Martin, *Nature*, **166**, 474 (1950).

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[7] All melting points are uncorrected. Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn. The 4,4'-biphenol was a gift of the Dow Chemical Company.

TABLE I

4,4′-BIPHENOL ESTERS

Diester, 4,4′-biphenol	Yield, %	M.P.	Recrystn. Solvents	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
Diacetate	61.8	161–162.5[a]	Benzene	71.10	70.97	5.22	5.37
Dipropanoate	77	148–149	Ethanol	72.47	72.57	6.08	5.95
Dibutanoate	62.5	123–123.5	Ethanol	73.60	73.73	6.79	6.70
Dipentanoate	21	118–119	Ethanol	74.55	74.37	7.34	7.35
Dihexanoate	73	116–117	Ethanol	75.37	75.37	7.90	8.13
Diheptanoate	21.8	118–118.5	Ethanol	76.06	75.83	8.35	8.48
Dioctanoate	63	121.5–123	Ethanol	76.67	76.52	8.74	8.54
Dinonanoate	65	120–121.5	Ethanol	77.21	77.07	9.07	9.03
Didodecanoate	70	122.5–124[b]	1:1 Dioxane-ethanol	78.50	78.33	9.88	9.84
Dibenzoate	77	251–252[c]	Dioxane	79.17	79.09	4.60	4.65

[a] Reported m.p. 159–160[4b]; 159–160[8a]; 160–161[8b]; 160.5–161.5[8c]; 163–164[8d]. [b] Reported m.p. 119.5–120.5.[4b]. [c] Reported m.p. 240–241[4b]; 250.5–251.5[8d]; 241[9a]; 257[9b].

TABLE II

3,3′-DIACYL-4,4′-BIPHENOLS

3,3′-Diacyl-4,4′-biphenols	Yield, %	M.P.	Recrystn. Solvents	Carbon, %		Hydrogen, %		Infrared Bands, μ	
				Calcd.	Found	Calcd.	Found	3.32–3.46	6.10–6.14
3,3′-Diacetyl	19.2	215–216[b]	1:1 Ethanol-dioxane	71.10	71.07	5.22	5.36	3.35	6.10
3,3′-Dipropanoyl	58	143–144[c]	Ethanol	72.47	72.54	6.08	6.00	3.37	6.10
3,3′-Dibutanoyl	89	125–126	1:1 Ethanol-dioxane	73.60	73.72	6.79	6.72	3.33	6.10
3,3′-Dipentanoyl	92.2	70–80.5	Ethanol	74.55	74.60	7.39	7.45	3.32	6.10
3,3′-Dihexanoyl	53.3	92.5–93.5	Ethanol	75.37	75.33	7.90	7.78	3.44	6.11
3,3′-Diheptanoyl	52.4	93–94	Ethanol	76.06	75.88	8.35	8.27	3.45	6.12
3,3′-Dioctanoyl	88	88.5–90	Ethanol	76.67	76.74	8.74	8.65	3.45	6.11
3,3′-Dinonanoyl	72	72–73	Ethanol	77.21	77.13	9.07	8.99	3.46	6.12
3,3′-Didodecanoyl	85	87–88	2:1 Ethanol-dioxane	78.50	78.46	9.88	9.64	3.45	6.12
3,3′-Dibenzoyl	30[a]	184–185	1:1 Ethanol-dioxane	79.17	79.28	4.60	4.62	3.35	6.14

[a] Reaction mixture heated for 3 days. [b] Reported m.p. 219–219.5[4a]; 219–220.[4b] [c] Reported m.p. 140–141.[4a]

ml. of dry chlorobenzene in a 200-ml. round bottom flask fitted with a thermometer and reflux condenser attached to a Gilman trap filled with sulfuric acid. The exit of the Gilman trap led to a water trough which served to absorb the hydrogen chloride evolved during the reaction. The flask was heated to 80° by means of a heating mantle during which time the vigorous evolution of hydrogen chloride was observed. The solution was heated at 80° overnight and then cooled. The light brown crystalline material which formed was recrystallized from benzene to give 8.35 g. (61.8%) of a white crystalline material, m.p. 161–162.5°.

B. *3,3′-Diacyl-4,4′-biphenols.* All runs were made with the same molar proportions and in the same general manner as described for 3,3′-diacetyl-4,4′-biphenol. The apparatus was the same as just described for the preparation of 4,4′-biphenol diacetate. Pertinent information is assembled in Table II.

3,3′-Diacetyl-4,4′-biphenol. A mixture of 4,4′-biphenol diacetate (5.2 g., 0.02 mol.), aluminum chloride (6.7 g., 0.05 mol.) and 50 ml. of dry chlorobenzene was heated at reflux for 24 hr. During this time hydrogen chloride was evolved and a dark yellow precipitate formed. The yellow mixture was cooled in an ice bath and 50 ml. of 3*N* hydrochloric acid was added dropwise with vigorous stirring. The chlorobenzene was then removed by steam distillation and the light brown solid remaining in the distillation flask was collected and recrystallized from 1:1 ethanol-dioxane to give 1.0 g. (19.2%) of light yellow fibrous needles, m.p. 215–216°.

C. *Infrared spectra.*[10] The infrared spectra of all the bis(*o*-hydroxyketones) were obtained in chloroform solution using sealed liquid absorption cells of approximately 0.1 mm. thickness. A Perkin-Elmer Model 21 double beam spectrophotometer with sodium chloride optics was used. Important absorption bands are listed in Table II.

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(10) The infrared spectra were run by Mrs. Ann. V. Baker of this laboratory.