yielded 3.25 g. of the γ-methoxy acid melting at 201° and crystallizing in small rhombic plates.

Anal. Calcd. for $C_{17}H_{18}O_5$: C, 67.5; H, 6.0; OCH_3, 10.3. Found: C, 67.6; H, 6.3; OCH_3, 10.0.

The chloroform solution, on suitable treatment, yielded 0.18 g. of a dimethoxy acid which by recrystallization from very dilute alcohol was obtained in fine needles melting at 148–149°.

Anal. Calcd. for $C_{18}H_{20}O_5$: C, 68.3; H, 6.4; OCH_3, 19.6. Found: C, 68.2; H, 6.5; OCH_3, 19.0.

This same dimethoxy acid was obtained by intensive methylation of the gamma methoxy acid, but the yield was exceedingly small.

Summary

This paper contains a description of the preparation, oxidation, reduction, alkylation and acylation of α,γ-diphenyl dihydroxy butyro lactone.

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Chloro Derivatives of Benzyl Phenols. II. Some Monochloro, Dichloro and Trichloro Derivatives of Ortho and Para Benzyl Phenols

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Continuing our studies on the benzylation of phenols, we have prepared chloro derivatives of ortho and para benzylphenols. A number of the dichloro derivatives of ortho and para benzylphenols have been described in an earlier article from this Laboratory.[1]

Condensations by means of aluminum chloride were carried out according to the technique previously described.[1,2] The mole proportions of reactants used were: one of benzyl chloride (or alcohol), three of phenol and one-half of aluminum chloride except in cases where 2,6-dichlorophenol was a reactant when the phenol and benzyl chloride were used in the ratio of one to one.

Temperatures between 20 and 35° were found to be satisfactory. In some cases with 2,6-dichlorophenol condensation failed to take place at lower temperatures.

In all cases the distillate from the ether extract was examined for benzyl ethers by dissolving in Claisen's alcoholic potash[3] and extracting with petroleum ether. The phenols were then liberated by treatment with hydrochloric acid and again extracted with ether.

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[1] Huston and Eldridge, THIS JOURNAL, **53**, 2260 (1931).

[2] Huston and others, *ibid*, **46**, 2775 (1924); **49**, 1366 (1927); **52**, 448 (1930); **53**, 2379 (1931); **54**, 1506 (1932).

[3] Claisen, *Ann.*, **442**, 224 (1924).

Condensations with Benzyl Alcohol (or Chloride).—Benzyl alcohol (or chloride) with 2-chlorophenol, by the aluminum chloride method, gave 4-hydroxy-3-chlorodiphenylmethane and 2-hydroxy-3-chlorodiphenylmethane.

The benzylation of 2-chlorophenol by the Claisen method[4] gave 2-hydroxy-3-chlorodiphenylmethane and 2-chlorophenyl benzyl ether. When 2-hydroxy-3-chlorodiphenylmethane and 4-hydroxy-3-chlorodiphenylmethane[5] were chlorinated in chloroform solution, they yielded 2-hydroxy-3,5-dichlorodiphenylmethane and 4-hydroxy-3,5-dichlorodiphenylmethane,[1] respectively.

The benzylation by the Claisen method of 4-chlorophenol yielded 2-hydroxy-5-chlorodiphenylmethane and 4-chlorophenyl benzyl ether while further attempts to benzylate the 2-hydroxy-5-chlorodiphenylmethane resulted in the formation of 4-chloro-2-benzylphenyl benzyl ether. Direct chlorination of 2-hydroxy-5-chlorodiphenylmethane gave 2-hydroxy-3,5-dichlorodiphenylmethane.[1] Benzylation by aluminum chloride of 4-chlorophenol gave 2-hydroxy-5-chlorodiphenylmethane.

Condensation with Chlorobenzyl Chloride.—Phenol was condensed with 2-chlorobenzyl chloride, 3-chlorobenzyl chloride and 4-chlorobenzyl chloride by the Claisen and aluminum chloride methods.

As a means of determining the structure of the compounds prepared, condensations of each of the chloro substituted benzyl chlorides were made with 2,4-dichlorophenol by the Claisen method and with 2,6-dichlorophenol by the aluminum chloride method. The trichlorobenzylphenols obtained by these condensations were then prepared by the cold chlorination of the corresponding monochlorobenzylphenols in chloroform. In no case was it possible to introduce chlorine into the benzyl nucleus, the chlorine entering only in the unoccupied ortho or para positions in the phenolic ring.

Claisen Method.—Phenol with 2-chlorobenzyl chloride in toluene yielded 2 hydroxy-2′-chlorodiphenylmethane and 2-chlorobenzyl phenyl ether; phenol with 3-chlorobenzyl chloride yielded 2-hydroxy-3′-chlorodiphenylmethane and 3-chlorobenzyl phenyl ether; phenol with 4-chlorobenzyl chloride yielded 2-hydroxy-4-chlorodiphenylmethane and 4-chlorobenzyl phenyl ether.

The treatment of 2,4-dichlorophenol in toluene with 2-chlorobenzyl chloride gave 2-hydroxy-3,5,2′-trichlorodiphenylmethane and 2-chlorobenzyl 2,4-chlorophenyl ether; 2,4-dichlorophenol and 3-chlorobenzyl chloride yielded 2-hydroxy-3,5,3′-trichlorodiphenylmethane and 3-chlorobenzyl 2,4-dichlorophenyl ether; 2,4-dichlorophenol with 4-chlorobenzyl chloride yielded 2-hydroxy-3,5,4′-trichlorodiphenylmethane and 4-chlorobenzyl 2,4-dichlorophenyl ether.

Aluminum Chloride Method.—Phenol with 2-chlorobenzyl chloride yielded 4-hydroxy-2′-chlorodiphenylmethane and 2-hydroxy-2′-chlorodiphenylmethane; phenol with 3-chlorobenzyl chloride yielded 4-hydroxy-3′-chlorodiphenylmethane; phenol with 4-chlorobenzyl chloride yielded 4-hydroxy-4′-chlorodiphenylmethane.

The condensation of 2,6-dichlorophenol with 2-chlorobenzyl chloride yielded 4-hydroxy-3,5,2′-trichlorodiphenylmethane; with 3-chlorobenzyl chloride it yielded 4-hydroxy-3,5,3′-trichlorodiphenylmethane; and with 4-chlorobenzyl chloride, 4-hydroxy-3,5,4′-trichlorodiphenylmethane.

In no case was the chlorobenzyl ether of any of the above phenols obtained in the aluminum chloride condensations. It will be observed that an ortho substituted product was produced along with the para benzylated phenol in the aluminum chloride condensation of phenol and 2-chlorobenzyl chloride. We were not able to isolate ortho substitution products in either the condensation of phenol with 3-chlorobenzyl chloride or phenol with 4-chlorobenzyl chloride. In the first case the boiling points of 2-hydroxy-3′-chlorodiphenylmethane and 4-hydroxy-3′-chlorodiphenylmethane did not differ enough

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(4) Claisen, *Ann.*, **442**, 221 (1924).

(5) Peratoner, *Gazz. chim. ital.*, **28**, I, 197–240 (1898).

to permit efficient separation by fractional distillation. (A rather low initial melting point of the esters of 4-hydroxy-3′-chlorodiphenylmethane would indicate the formation of a small amount of the ortho isomer.) In the second case, there was apparently none formed for both 2-hydroxy-4′- and 4-hydroxydiphenylmethane were solid crystalline substances which were definitely isolable.

Condensations in Methyl Alcohol.—The 2-chlorobenzyl phenyl ether, 3-chlorobenzyl phenyl ether and 4-chlorobenzyl phenyl ether were prepared by heating phenol and the various monochlorobenzyl chlorides in the presence of sodium methylate in methyl alcohol. Similarly, 2-chlorobenzyl 2,4-dichlorophenyl ether, 3-chlorobenzyl 2,4-dichlorophenyl ether and 4-chlorobenzyl 2,4-dichlorophenyl ether were prepared by the condensation of 2,4-dichlorophenol with 2-chlorobenzyl chloride, 3-chlorobenzyl chloride and 4-chlorobenzyl chloride, respectively.

These ethers were found to be identical with those obtained in the Claisen condensation.

Comparison of Yields.—In the Claisen condensations the yields of the benzylated phenols arranged in the order of descending magnitude were 2-hydroxy-5-chlorodiphenylmethane 43.4%, 2-hydroxy-3-chlorodiphenylmethane 27%, 2-hydroxy-4′-chlorodiphenylmethane 25%, 2-hydroxy-2′-chlorodiphenylmethane 16.71% and 2-hydroxy-3′-chlorodiphenylmethane 7.78%. In the case of the 2-hydroxy-3′-chlorodiphenylmethane the yield was increased about five-fold by adding 30 g. of 3-chlorobenzyl chloride to the reaction mixture of half mole quantities. These yields were in the order expected from consideration of the hydrolysis rates[6] of these and analogous bromine compounds and the yields from the corresponding bromobenzyl chlorides.[7]

The 4-hydroxy-2′-chlorodiphenylmethane, 4-hydroxy-4′-chlorodiphenylmethane and 4-hydroxy-3′-chlorodiphenylmethane obtained from aluminum chloride condensations were obtained in yields of 14.74, 15.84 and 46%, respectively.

The yields where given of the trichloro derivatives formed by condensing the various chlorobenzyl chlorides with 2,4-dichlorophenol by the Claisen method and with 2,6-dichlorophenol by the aluminum chloride reaction appear to be in the same order but less than in the condensations with unsubstituted phenol. This fact points to a decrease in activity where the phenolic ring is substituted with chlorine.

TABLE I

CHLORO DERIVATIVES OF BENZYLPHENOLS

Compound Chlorodiphenylmethane	Crystalline structure	M. p., °C.	Yield, %	Chlorine, % Found	Chlorine, % Calcd.
2-Hydroxy-2′-	Light green oil. On standing, pink	B. p. 146–151 (3 mm.)	16.21	16.88	16.22
2-Hydroxy-3-	White soft needles from pet. ether	40.5–41.5	27	15.89	16.22
2-Hydroxy-3′-	Brownish oil	B. p. 192–194(14 mm.)	7.78	16.38	16.22
2-Hydroxy-5-[8]	White needles from alc.	48–49	43.4	16.11	16.22
2-Hydroxy-4′-[8]	Needles in rosets from alc.	60–61	25	16.37	16.22
4-Hydroxy-2′-	White needles from ligroin	68–69	14.74	15.95	16.22
4-Hydroxy-3-	Oil	B. p. 145–148(3 mm.)	40	16.09	16.22
4-Hydroxy-3′-	Brownish oil	B. p. 200–202(14 mm.)	15.84	16.00	16.22
4-Hydroxy-4′-[8]	Needles in rosets from ligroin	87–87.5	46	16.06	16.22
2-Hydroxy-5,4′-di-	Oily crystals	44.5–45.5	15	25.63	26.9
2-Hydroxy-3,5,2′-tri-	Needles in rosets from alc.	59.5–60.5		36.75	37.01
2-Hydroxy-3,5,3′-tri-	Flakes from pet. ether	59.4–60	4.56	36.89	37.01
2-Hydroxy-3,5,4′-tri-	Fine needles from alc.	69.5–70.5		36.94	37.01
4-Hydroxy-3,5,2′-tri-	White needles from ligroin	86.5–87.5	16.8	36.81	37.01
4-Hydroxy-3,5,3′-tri-	Short white needles from pet. ether	79–80	11.52	36.95	37.01
4-Hydroxy-3,5,4′-	Long needles from pet. ether	61.5–62.5	35	36.99	37.01

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(6) Oliver, *Rec. trav. chim.*, **49**, 698–997 (1930).

(7) Huston and others, THIS JOURNAL, **55**, 2146 (1933).

(8) Klarmann, Gates and Shternov, *ibid.*, **54**, 3323 (1932).

TABLE II

CHLORO DERIVATIVES OF BENZYL PHENYL ETHERS

Compound Ether	Crystalline structure from alcohol	M. p., °C.	Yield, %	Chlorine, %	
				Found	Calcd.
2-Chlorobenzyl phenyl	Oil	B. p. 140–145(2.5 mm.)		15.51	16.22
3-Chlorobenzyl phenyl	Transparent plates	36–36.4	10.89	16.20	16.22
4-Chlorobenzyl phenyl	Plate-like crystals	85.5–86.5	5.8	15.84	16.22
4-Chlorobenzyl-4-chlorophenyl	Needles	80–81	3	28.01	27.83
2-Chlorobenzyl-2,4-dichlorophenyl	White needles	61–62		36.78	37.01
3-Chlorobenzyl-2,4-dichlorophenyl	Long white needles	42–42.5	1.46	37.2	37.01
4-Chlorobenzyl-2,4-dichlorophenyl	Needles from alc.	64.5–65.5	2.6	36.40	37.01
2-Chlorophenyl benzyl	Yellow oil	B. p. 138–140(3 mm.)	7.5	15.75	16.24
4-Chlorophenyl benzyl	Long white needles	70–71	7.3	15.64	16.23
4-Chloro-2-benzylphenyl benzyl	Lustrous plates	53–54	59	11.13	11.49

TABLE III

ESTERS OF THE VARIOUS PHENOL DERIVATIVES PREPARED ACCORDING TO THE METHOD OF EINHORN AND HOLLAND[9]

Benzoyl ester of chlorodiphenylmethane	Crystalline structure from alcohol	M. p., °C.	Chlorine, %	
			Found	Calcd.
2-Hydroxy-2′-	Yellow oil	B. p. 173–176(2.5 mm.)	10.81	11.00
2-Hydroxy-3-	Large oblong crystals	69–71	11.18	11.007
2-Hydroxy-3′-	White flakes	67–67.4	11.13	11.00
2-Hydroxy-5-	White needles	54–55	10.81	11.00
4-Hydroxy-2′-	White flakes	64.5–65.5	11.10	11.00
4-Hydroxy-3-	Small thin flakes	71–73	11.00	11.007
4-Hydroxy-3′-	Fine needles	57.5–58.0	10.96	11.00
4-Hydroxy-4′-	Large white needles	115–116	10.93	11.00
2-Hydroxy-5,4′-di-	Prismatic plates	84.5–85.5	19.9	19.78
2-Hydroxy-3,5,2′-tri-	Fine white needles	81–82	27.00	27.17
2-Hydroxy-3,5,3′-tri-	Fine white needles	63.5–64.0	27.14	27.17
4-Hydroxy-3,5,2′-tri-	Small white needles	86–87	27.43	27.17
4-Hydroxy-3,5,3′-tri-	Flakes in rosets	130–130.4	27.46	27.17
4-Hydroxy-3,5,4′-tri-	White flakes	116–117	26.95	27.17
Benzene sulfonyl ester of chlorodiphenylmethane				
2-Hydroxy-3-	Coarse white needles	62–64	1.92	9.902
2-Hydroxy-5-	White needles	68–69	9.63	9.902
4-Hydroxy-3-	Granular crystals	65–68	9.677	9.902
2-Hydroxy-3,5,3′-tri-	Plates in clumps	114.5–115	24.85	24.88
p-Toluene ester of chlorodiphenylmethane				
2-Hydroxy-3-	Small white crystals	81.5–83.5	9.49	9.53
2-Hydroxy-5-	Flakes, white	75–75.5	9.28	9.53
4-Hydroxy-3-	Small granular	51–53	9.41	9.53
2-Hydroxy-3,5,3′-tri-	Coarse white needles	125.4–126	24.01	24.09
4-Hydroxy-3,5,3′-tri-	Coarse white needles	104.5–105	24.01	24.09

An absence of ether formation will be noted in all aluminum chloride condensations described in this paper. Since a large yield of 2,6-dichlorophenyl benzyl ether was obtained by condensing 2,6-dichlorophenol and benzyl chloride with aluminum chloride, these results were not expected. It is also worthy of note that the three monobromobenzy lchlorides[7] gave good yields of ethers when condensed under the same conditions with phenol but no ethers when condensed with bromophenols.

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[9] Einhorn and Holland, *Ann.*, **301**, **95** (**1898**).

These findings suggest a generalization to the effect that chlorine (unlike bromine) in the ring of benzyl chlorides is not favorable to ether formation.

Summary

Some monochloro, dichloro and trichloro derivatives of the benzylphenols and benzyl phenyl ethers were prepared.

No ethers were formed in the aluminum chloride condensations where chlorine was present in the nucleus of the benzyl chloride.

In the Claisen reaction the presence of chlorine in the nucleus of the benzyl chloride exerted a retarding influence on the yield of benzylated phenol and its corresponding ether, the greatest retarding effect being exhibited when the chlorine was in the meta position, the next when in the ortho and the least when in the para position.

The yields of the benzylated phenol by the Claisen reaction in case of meta substituted benzyl chloride was increased by adding the corresponding benzyl ether to the reaction mixture.

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Addition Reactions of Unsaturated Alpha-Ketonic Acids. III

BY MARIE REIMER AND HELEN H. KAMERLING

The reaction of bromine with benzalpyruvic acid and with its *p*-methoxy and *o*-methoxy substitution products has been described in earlier papers.[1] The reaction in every case was the same: addition of bromine to the ethylenic linkage of the side chain. The acids themselves, however, as well as their bromination products, differ in certain respects so strikingly that it seemed of value to continue the investigation of these compounds for the purpose of studying the effect of methoxyl groups in different positions in the benzene ring on the reactions of the molecule.

The present paper describes the preparation and reaction with bromine of benzalpyruvic acid in which a methoxyl group is in the meta position to the side chain. This is of interest not only for comparison with other unsaturated α-ketonic acids of this series but particularly in view of the behavior of *m*-methoxycinnamic acid on treatment with bromine. This is described by Davies and Davies[2] as substitution in the ring with no addition to the ethylenic linkage of the side chain. So unusual is this behavior of a cinnamic acid that one is justified in reading the conclusions of Davies and Davies with surprise and even with a certain measure of skepticism. We have repeated these experiments as described by Davies and Davies and also under other conditions of temperature and with several different

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[1] Reimer, THIS JOURNAL, **48**, 2454 (1926); Reimer and Howard, *ibid.*, **50**, 2506 (1928).

[2] Davies and Davies, *J. Chem. Soc.*, 602 (1928).