The material had a melting point of 168–175° and an infrared spectrum (potassium bromide pellet) identical with that of 2,4-dinitroaniline, lit.[15b] m.p. 180° (188°).

Oxidation of cyclohexylamine. Excess cyclohexylamine was added to a solution of chromic anhydride in 12*N* sulfuric acid, and the mixture was allowed to stand overnight at room temperature. The color of the mixture changed from orange to murky brown. The mixture was extracted with ether, the ether solution was dried with magnesium sulfate, and the ether was removed by distillation. The residue, which was water white, was added to a solution of 2,4-dinitrophenylhydrazine in aqueous perchloric acid.[13] The orange crystals had a melting point of 110–130°. After two recrystallizations from ethanol, the crystals had a melting point of 122–142°. Paper chromatography of the mixture of 2,4-dinitrophenylhydrazones, using acetone-hexane as the eluent, resolved the mixture into two components. One component was red and did not move appreciably on the chromatograph. The other component moved at the same rate as cyclohexanone 2,4-dinitrophenylhydrazone.

Oxidation of N-t-butyl-2,4-dinitroaniline (III). A heterogeneous mixture of 0.50 g. (2.1 mmoles) of III, 0.50 g. (5.0 mmoles) of chromic anhydride, and 50 ml. of 12*N* sulfuric acid, through which was passed a slow stream of nitrogen, was heated in an oil bath at 115° for 1 hr. The effluent gases were passed into 25 ml. of cold carbon tetrachloride. The reaction mixture changed in color from orange to dark green during the heating period, and the carbon tetrachloride solution rapidly decolorized bromine. The reaction mixture was poured on 50 g. of crushed ice, and the yellow solid that separated was collected and recrystallized from aqueous acetone. It weighed 0.30 g. (1.6 mmoles, 80%), m.p. 171–179°, and had an infrared spectrum identical with that of 2,4-dinitroaniline.

2,4-Dinitrophenol from 2,4-dinitroaniline. A mixture of 1.00 g. (5.5 mmoles) of 2,4-dinitroaniline, m.p. 184–185°, and 60 ml. of 12*N* sulfuric acid was distilled until 40 ml. of distillate was collected. The yellow solid (2,4-dinitrophenol) that steam distilled was collected and recrystallized from methanol. It weighed 0.40 g. (2.2 mmoles) and had a melting point of 109.5–110.3°. The residue in the reaction flask was poured into 20 ml. of ice water, and the resulting mixture was made alkaline by the careful addition of cold 6*N* sodium hydroxide. The alkaline solution was extracted with 50 ml. of ether, the ether was evaporated, and the residue was recrystallized from aqueous acetone. The recrystallized material weighed 0.12 g., m.p. 166–170°, and had an infrared spectrum (potassium bromide pellet) superimposable on that of 2,4-dinitroaniline.

Acknowledgment. The availability of the NMR spectrometer used in this research was made possible by a grant (CY-5528) from the Public Health Service.

DAVIS, CALIF.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE PAINT DIVISION, PITTSBURGH PLATE GLASS CO., AND S. C. JOHNSON & SON, INC.]

The Condensation of Pyruvic Acid with Phenols[1]

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The condensation of pyruvic acid with phenol in sulfuric acid was reinvestigated. Contrary to the report of Böttinger,[3] the product was found to be not 2,2′-bis(*p*-hydroxyphenyl)propionic acid (Ia) but rather a polymeric material whose possible structure is discussed. Authentic Ia was prepared from phenol and pyruvic acid in acetic acid with hydrogen chloride catalyst. The dimethyl ether of Ia was synthesized unequivocally by oxidation of 3,3′-bis(*p*-methoxyphenyl)-2-butanone with sodium hypochlorite. The condensation of pyruvic acid with certain substituted phenols was also investigated, and the nature of the products is discussed.

It has been reported by Böttinger[3] that the addition of phenol to a solution of pyruvic acid in concentrated sulfuric acid near 0° afforded "diphenopropionic acid," presumably compound Ia. Other phenols and phenolic ethers were claimed to react similarly. Diphenopropionic acid was described as a granular, amorphous white solid, insoluble in benzene and chloroform, but soluble in acetone, ethyl acetate, and in bases. It did not melt below 268° but decomposed at elevated temperatures. The carbon and hydrogen analyses appeared to fit the formula for Ia as a monohydrate. Bromination in chloroform solution gave a bromo derivative alleged to have the formula $C_{15}H_{12}Br_2O_4$.

The condensation of pyruvic acid with phenol was reinvestigated. By following Böttinger's procedure a substance was obtained whose properties were in good agreement with those reported. The evidence showed distinctly, however, that the substance was not 2,2′-bis(*p*-hydroxyphenyl)propionic acid (Ia). Furthermore, authentic Ia was prepared and its structure established by an unequivocal synthesis. Bromination by the method[4] of Ingberman resulted in the uptake of 1.5 atoms of bromine based on Ia.

Doubts as to the assigned structure of Ia became evident when (1) it was observed that the infrared spectrum displayed a strong lactone band at 1800 cm.$^{-1}$ in addition to the carboxyl band at 1695 cm.$^{-1}$, (2) a lack of a definite melting point was observed, and (3) an uptake of only 1.5 atoms of bromine per mole was found when it would be

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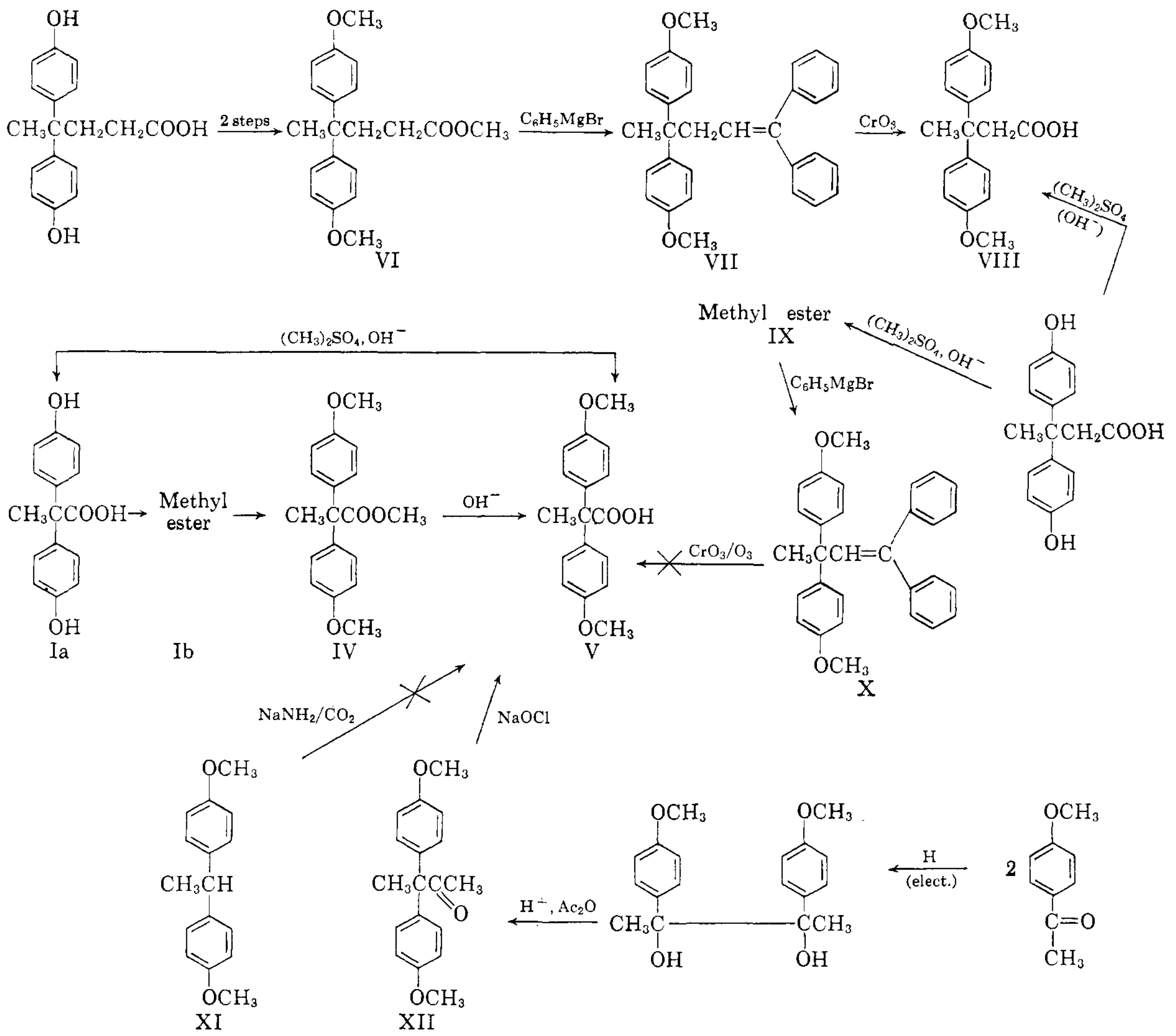
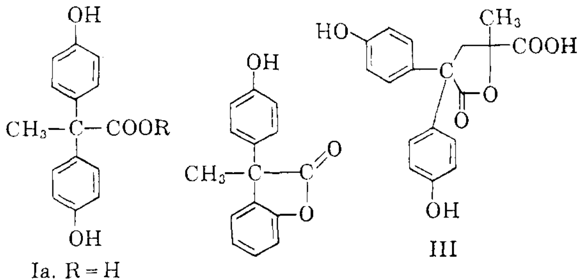
(3) C. Böttinger, *Ber.*, **14**, 1595 (1881); *Ber.*, **16**, 2071 (1883).

(4) A. K. Ingberman, *Anal. Chem.*, **30**, 1003 (1958).



expected to be at least 4.0. Several possibilities were thereby suggested. If some *ortho* substitution had occurred, the product could be a mixture of Ia with the phenolic lactone II. Also it is known that pyruvic acid undergoes an aldol condensation in acidic medium,[5,6] and reaction of the aldol with


Ia. R = H
Ib. R = CH_3
II
III

phenol would give rise to compound III for which the analytical, solubility, and spectral data were in good accord. However, Rast and ebullioscopic data indicated that the material is probably polymeric with a molecular weight in the range of 1300–1350. Efforts were then made to prepare Ia by alternate procedures.

When pyruvic acid was allowed to react with excess phenol in acetic acid saturated with dry hydrogen chloride for several days at 35–65°, there was obtained 40–50% yield of a crystalline solid, melting at 177.5–179°, which gave a correct analysis for Ia containing one-half mole of benzene of crystallization. Esterification in methanol gave the methyl ester Ib, m.p. 129–130°. Treatment of Ib with methyl sulfate in alkali gave the dimethyl ether IV, m.p. 75.5–76.5°, which was saponified to the 2,2-bis(*p*-methoxyphenyl)propionic acid (V), m.p. 104–105°. Alternatively, V was prepared directly by methylation of Ia. To prove the structure of V, methyl 4,4-bis(*p*-hydroxyphenyl)pentanoate[7] was converted to the dimethyl ether methyl ester VI. Reaction of VI with phenylmagnesium bromide gave the olefin VII which, upon treatment with chromic acid, gave 3,3-bis(*p*-methoxyphenyl)-

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(5) L. Wolff, *Ann.*, **317**, 1 (1901).

(6) A. W. K. De Jong, *Rec. trav. chim.*, **21**, 191 (1902).

(7) A. R. Bader and A. D. Kontowicz, *J. Am. Chem. Soc.*, **76**, 4465 (1954).

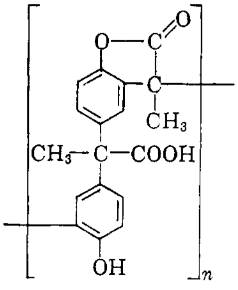
butanoic acid (VIII). At about the time VIII was prepared, a publication by Yu and Day[8] described the preparation of 3,3-bis(*p*-hydroxyphenyl)butanoic acid and its ethyl ester by condensation of phenol with ethyl acetoacetate. The phenolic acid of Yu and Day was converted to the dimethyl ether VIII in the usual way. The methyl ester of VIII (IX) was treated with phenylmagnesium bromide to give a compound which gave a correct analysis for the olefin X. However, all efforts to oxidize X to 2,2-bis(*p*-methoxyphenyl)propionic acid with chromic acid or ozone were unsuccessful. In all cases the olefin was either recovered unchanged or was degraded to anisic acid.

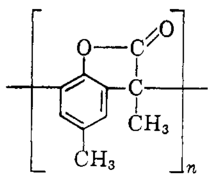
Another approach to the preparation of V was an effort to carboxylate the anion of 1,1-dimethoxyphenylethane (XI). However, despite several variations in procedure there was no evidence for carbanion formation,[9] and XI was recovered unchanged.

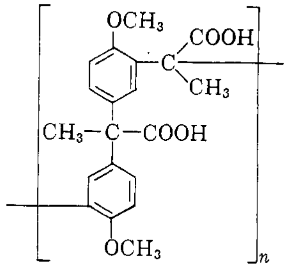
The 2,2-bis(*p*-methoxyphenyl)propionic acid (V) was finally prepared unequivocally by the oxidation of 3,3-bis(*p*-methoxyphenyl)-2-butanone (XII)[10] with sodium hypochlorite solution.

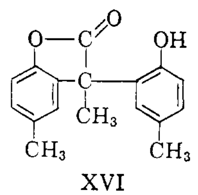
It is therefore apparent that Böttinger did not prepare Ia as alleged. Possibly an evanescent diphenopropionic acid intermediate is formed, but this could not be isolated. In the presence of the excess of pyruvic acid it is likely that condensation occurs further through the *ortho* or *para* positions of the phenol ring. It is possible that the presence of a carboxyl group adjacent to the carbonyl group in pyruvic acid exerts an activating influence and, therefore, pyruvic acid behaves more as an aldehyde in its reaction with phenol in highly acidic medium. As evidence it was found that 2,2-bis-(*p*-hydroxyphenyl)propionic acid Ia reacted with excess pyruvic acid under Böttinger's conditions to give a nearly quantitative yield of a polymer whose properties were quite similar to those of the Böttinger material. Finally, evidence that polymer formation occurred through the *ortho* positions may be inferred from an experiment with 2,6-xylenol in which the *ortho* positions are blocked. In this case only the simple condensation product, 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propionic acid, m.p. 202–203° was obtained.

A number of structures may be written for Böttinger's polymer, but XIII appears to be most in accord with experimental data based on (1) selective bromination for determining the number of unsubstituted positions in phenolic nuclei *ortho* or *para* to phenolic hydroxyl[11]; (2) reaction of *p*-cresol with pyruvic acid which gave a polymer XIV having only the lactone band at 1800 cm.$^{-1}$ and no carboxyl absorption; (3) reaction of anisole with pyruvic acid which gave a polymer XV exhibiting no lactone absorption but having the carboxyl band at 1695 cm.$^{-1}$; and (4) the reaction of Ia with pyruvic acid to give a polymeric substance similar to Böttinger's material in terms of infrared spectrum, neutralization equivalent, and bromine number (see footnote[11] and Experimental).


XIII


XIV


XV


XVI

EXPERIMENTAL[12]

Materials. Pyruvic acid, obtained from Matheson, Coleman, and Bell, was redistilled before use, b.p. 50–53° (5

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(8) A. Yu and A. R. Day, *J. Org. Chem.*, **23**, 1004 (1958).

(9) J. Weinstock and S. N. Lewis, *J. Am. Chem. Soc.*, **79**, 6243 (1957), readily prepared the carbanion of 1,1-diphenylethane from sodium amide in ether, a procedure which failed in the present case. Electron-releasing groups on the aromatic ring may increase the electron density at the tertiary carbon atom. Therefore, 1,1-dimethoxyphenyl ethane may be a weaker acid than 1,1-diphenylethane. Also, compare R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 2325 (1947), on formation of carbanions from diphenylmethane.

(10) C. C. Price and G. P. Mueller, *J. Am. Chem. Soc.*, **66**, 634 (1944).

(11) Expansion of formula XIII in a regular manner to a molecular weight of 1300–1400 indicates the presence of 7 active sites (*ortho* or *para* to free phenolic hydroxyls) available for bromination. The number actually found experimentally was 7.8 atoms of bromine per mole based on a molecular weight of 1338. This corresponds to 1.5 atoms of bromine per mole of Ia. The validity of the procedure was proved by bromination of Ia and XVI as model compounds whereby 3.9 and 1.15 atoms of bromine were absorbed, respectively. Since the molecular weight of the product from the reaction of Ia and pyruvic acid could not be determined, its bromination data has been expressed in terms of a bromine number, *i.e.*, millequivalents of bromine per gram of sample. For Ia, calcd. 2481; found: 2421 and 2424. For Böttinger's material, found: 927 and 933. For Ia + pyruvic acid reaction product, found: 715 and 695.

(12) All boiling points and melting points are uncorrected. Carbon and hydrogen analyses were carried out by Micro-Tech Laboratories, Skokie, Ill., and Galbraith Laboratories, Knoxville, Tenn. Ebullioscopic molecular weight determinations were carried out by Organalysis, Barrington, Ill. We are indebted to Dr. James B. Lear and Miss Ruth S. Johnston of the Pittsburgh Plate Glass Co. and Messers. Harry H. Gloyd and Lee R. Williamson of S. C. Johnson & Sons, Inc. for the infrared and ultraviolet absorption spectra.

mm.). U.S.P. Phenol and cresol were freshly distilled before use. Anisole and 2,6-xylenol were used without further purification. Pyridine was AR grade, dried over potassium hydroxide and distilled.

Böttinger's reaction of pyruvic acid with phenol. Eighty-eight grams (1.0 mole) of pyruvic acid was added dropwise over a 1-hr. period to 600 ml. of concd. sulfuric acid cooled to −10°. After the solution was stirred an additional 45 min., 188 g. (2.0 moles) of phenol was added in small portions at the same temperature. With each addition the color turned red momentarily, then faded to yellow. After addition of the phenol was complete (2.5 hr.), the temperature was held at −5 to −10° for an additional 6 hr., and the mixture was then poured over crushed ice. The pink solid was washed with ice water, then dissolved in 10% sodium bicarbonate solution, followed by extraction with 50:50 ether–ethyl acetate mixture to remove unchanged phenol. The product was reprecipitated by slow addition of the bicarbonate solution to a mixture of 1 part of hydrochloric acid and 3 parts of water at about 70°. The light yellow or tan precipitate was filtered, washed thoroughly with water, then dried *in vacuo* over sulfuric acid. The yield was 102.7 g. (39.8%) based upon phenol.

The material did not melt sharply in a capillary tube, but rather began to decompose at 240°.

Anal. Calcd. for $C_{15}H_{14}O_4 \cdot H_2O$: C, 65.21; H, 5.80. Found (by Böttinger): C, 64.8, 65.5, 66.09; H, 5.8, 5.61, 5.16. Found (this work): C, 66.54, 66.73; H, 5.27, 5.49; mol. wt. (b.p. in acetone), 1338; (Rast), 1343, 1305. Neut. equiv., 403.7. Infrared maximum at 1800 cm.$^{-1}$ (5-membered lactone) and 1695 cm.$^{-1}$ COOH (Nujol).

Functionality by selective bromination. The selective bromination procedure employed was essentially that of Ingberman.[4] Since the Böttinger product proved to be only partially soluble in the acetic acid–pyridine reaction medium, the solvent modification of a 1:1 mixture of acetic acid and dimethylformamide, suggested by the author, was employed. A sample approximately equivalent to 3 milliatoms of bromine was weighed into an iodine flask followed by a 1:1 mixture of acetic acid and dimethylformamide. After solution of the sample was effected, 25 ml. of a 0.15*M* solution of bromine in glacial acetic acid was introduced from a pipette followed by addition of 1 ml. of a 27% solution of pyridine in glacial acetic acid. The mixture was allowed to stand for 15 min. A minimum of 5 ml. of 50% aqueous potassium iodide was added, and the liberated iodine was titrated in the usual manner with 0.1544*M* sodium thiosulfate. A blank was run in the same manner. In order to be certain that the procedure was valid for determination of the phenol functionality of the Böttinger substance, phenol, Ia, and XVI were analyzed. Phenol AR Grade, calcd. Br consumption (atoms/mole), 3.0; found, 2.96 (99.0% of theory). Ia, calcd. Br consumption (atoms/mole), 4.0; found, 3.91 (97.7% of theory). Böttinger's substance, found, 7.8 atoms/mole based on a molecular weight of 1338. XVI, calcd. Br consumption (atoms/mole) 1.0; found, 1.15.

2,2-Bis(p-hydroxyphenyl)propionic acid (Ia). A mixture of 470 g. (5.0 moles) of phenol and 88.0 g. (1.0 mole) of pyruvic acid in 500 ml. of glacial acetic acid was saturated with anhydrous hydrogen chloride during which time the temperature rose spontaneously to 65°. After cooling, the flask contents were allowed to stand at room temperature for 24 hr. after which the mixture was again saturated with hydrogen chloride for 2 hr. longer. After 3 days, the mixture was poured over crushed ice and the oil extracted with ethyl acetate. The aqueous phase was discarded, and the organic phase was washed with saturated sodium chloride solution until the washings were neutral. The product was then extracted with saturated sodium bicarbonate solution and the organic phase rejected. The aqueous solution was added slowly to an excess of dilute hydrochloric acid to give a light yellow oil which was then taken up in fresh ethyl acetate. The extract was washed with saturated sodium chloride solution until the washings were neutral and then dried over anhydrous calcium sulfate. The dried solution was concentrated to an amber oil which was treated with one liter of benzene and warmed to 70°. Enough ethyl acetate was added until the oil was just dissolved, and the mixture was then concentrated to about three fourths of its original volume. After having been allowed to stand for 3–5 days, the solution deposited a heavy crop of dense white crystals which were collected and washed sparingly with benzene, then with petroleum ether. After air-drying, there was obtained 120–150 g. (40–50%) of product, m.p. 177–179°. The analytical sample was prepared similarly by recrystallization from a mixture of benzene and ethyl acetate, m.p. 177.5–179°.

Anal. Calcd. for $C_{15}H_{14}O_4 \cdot {}^1/_2C_6H_6$: C, 72.71; H, 5.76; neut. equiv., 297.3. Found: C, 72.87, 73.07; H, 5.81, 5.94; neut. equiv., 299.

Methyl 2,2-bis(p-hydroxyphenyl)propionate (Ib). A solution of 75 g. (0.252 mole) of the above acid (Ia) was refluxed in 1000 ml. of dry methanol for 16 hr. while being saturated with a stream of dry hydrogen chloride. The product was isolated by conventional procedures and crystallized from benzene–petroleum ether to obtain 58.8 g. (86%) of crude product, m.p. 125.5–127°. The analytical sample, prepared by two recrystallizations from benzene and drying *in vacuo*, melted at 129–130°.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.52; 70.66; H, 6.02, 5.90.

Methyl 2,2-bis(p-methoxyphenyl)propionate (IV). Thirty grams of methyl sulfate was added dropwise to a mixture of 40.8 g. (0.15 mole) of methyl 2,2-bis(*p*-hydroxyphenyl)-propionate and a solution of 18 g. of sodium hydroxide in 300 ml. of water while the temperature was permitted to rise to 40°. A total of 150 g. (1.2 moles) of methyl sulfate and 54.0 g. (1.4 moles) of sodium hydroxide solution was added, while the *p*H was maintained at 9–10. A crude product was isolated by conventional procedures which gave, after distillation, 39.1 g. (87%) of a viscous, colorless distillate, b.p. 181–184° (0.3 mm.), which solidified in the receiver. After recrystallization from petroleum ether, the melting point was 75.1–75.5°.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.26, 72.11; H, 6.69, 6.70.

2,2-Bis(p-methoxyphenyl)propionic acid (V). A solution of 9.0 g. (0.03 mole) of methyl 2,2-bis(*p*-methoxyphenyl)propionate in 25 ml. of methanol and 50 ml. of water containing 12 g. (0.3 mole) of sodium hydroxide was refluxed for 16 hr. Work-up in the usual manner gave a residue which was dissolved in a mixture of ethyl acetate and petroleum ether, concentrated, and allowed to crystallize. There was obtained 7.2 g. (84%) of crystalline acid, m.p. 104–105°. The melting point was unchanged upon crystallization from a mixture of ethyl acetate and petroleum ether or benzene and petroleum ether.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.38, 71.52; H, 6.37, 6.21.

Methylation of 2,2-bis(p-hydroxyphenyl)propionic acid (Ia). The same product (V) was obtained in 49% yield from Ia by treatment with methyl sulfate and sodium hydroxide solution, m.p. 104.5° from ethanol.

Anal. Calcd.: Neut. equiv., 286.4. Found: 289.0.

Methyl 4,4-bis(p-methoxyphenyl)pentanoate (VI). By the procedure employed for the preparation of IV there was obtained from 150 g. (0.5 mole) of 4,4-bis(*p*-hydroxyphenyl)-pentanoate, 163 g. (99%) of nearly colorless oil, b.p. 208° (0.05 mm.).

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.05; sapon. equiv., 328.4. Found: C, 72.41, 72.49; H, 7.44, 7.65; sapon. equiv., 321.

Reaction of phenylmagnesium bromide with VI. *1,1-Diphenyl-4,4-bis(p-methoxyphenyl)-1-pentene* (VII). To 127 g. (0.7 mole) of phenylmagnesium bromide in 200 ml. of ether was added dropwise during *ca.* 30 min. a solution of 65.7 g. (0.20 mole) of the ester VI in 250 ml. of benzene. The mixture was refluxed for 10 hr. and allowed to stand at room temperature overnight. The product was isolated by decomposing with 50% sulfuric acid and working up in the conventional manner. The product crystallized from ether–petroleum ether (b.p. 30–60°). Filtration gave 72 g. (83%) of the olefin VII as a slightly yellowish solid, m.p. 83–86°. An analytical sample, m.p. 86.5–87.5° (soft at 84°), was prepared by several recrystallizations from a mixture of benzene and hexane.

Anal. Calcd. for $C_{31}H_{30}O_2$: C, 85.66; H, 6.96. Found: C, 85.29, 85.25; H, 7.08, 7.06.

Oxidation of 1,1-diphenyl-4,4-bis(p-methoxyphenyl)-1-pentene (VII). *3,3-Bis-(p-methoxyphenyl)butanoic acid* (VIII). To a solution of 15 g. (0.035 mole) of VII in 100 ml. of acetic acid was added at 60° over a period of 3 hr. a solution of 20.7 g. (0.21 mole) of chromic acid in 15 ml. of water and 100 ml. of acetic acid. The mixture was stirred at 60° for an additional 1 hr. Three grams of a brown solid was isolated which was crystallized from acetone–ether to give acid VIII, m.p. 160–164°, showing a carboxyl band at 1695 cm.$^{-1}$ Mixed m.p. with the acid (m.p. 161–162°) obtained from phenol and ethyl acetoacetate (*vide infra*) was 160–163°.

3,3-Bis(p-hydroxyphenyl)butanoic acid was obtained by the method of Yu and Day[8] in 61% yield. In contrast to the report of these authors the acid, either when recrystallized from benzene alone or from its mixture with ethyl acetate, had a m.p. 170.5–171.5° and was not solvated (reported m.p. of the solvate 150°).

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.6; H, 5.92. Found: C, 70.41, 70.67; H, 6.48, 6.24.

Methylation of 3,3-bis(p-hydroxyphenyl)butanoic acid. Methyl 3,3-bis(p-methoxyphenyl)butanoate (IX). To a solution of 136 g. (0.50 mole) of the above acid, m.p. 168–170°, in 60 g. (1.5 moles) of sodium hydroxide and 400 ml. of water there was added over a period of 3 hr. 208 g. (1.65 moles) of methyl sulfate. The resulting mixture was heated at 70° for 1 hr., the *p*H adjusted to 7, and the mixture heated at 70° for an additional 3 hr. Extraction with ether and distillation gave 123 g. (78.5%) of IX as a viscous oil, b.p. 195–205° (0.3 mm.), showing absorption at 1739 cm.$^{-1}$

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.6; H, 7.06; sapon. equiv., 314.4. Found: C, 72.23, 72.40; H, 7.06, 6.92; sapon. equiv., 312.3.

3,3-Bis(p-methoxyphenyl)butanoic acid (VIII). By the procedure employed for the preparation of V there was obtained 28 g. of a white powder, m.p. 154–158°. Recrystallization from a mixture of acetone and ether gave 26 g. (94%) of the acid VIII, m.p. 159–162°. The analytical sample, m.p. 161–162°, showing carboxyl at 1695 cm.$^{-1}$ was prepared by several recrystallizations from the same solvent.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.99; H, 6.71; neut. equiv., 300.3. Found: C, 72.17, 71.93; H, 6.49, 6.57; neut. equiv., 303.3.

Reaction of phenylmagnesium bromide with IX. *1,1-Diphenyl-3,3-bis(p-methoxyphenyl)-1-butene* (X). By a procedure similar to that employed for the preparation of VII there was obtained 38 g. (68%) of a nearly colorless solid, m.p. 115–124°, and about 10 g. of a brown oil. The latter was not investigated further. Numerous recrystallizations from a mixture of ethyl acetate and methanol gave X as a white solid, m.p. 128–130°. The analytical sample, m.p. 130–131° (softening at 129°), was prepared by recrystallization from the same solvent. The infrared spectrum did not show carboxyl or hydroxyl absorption. Ultraviolet spectrum (isooctane): λ_{max} 255 mμ; log ϵ_{max} 4.22.

Anal. Calcd. for $C_{30}H_{28}O_2$: C, 85.68; H, 6.71. Found: C, 85.11, 85.38; H, 6.72, 6.79.

Oxidation of 1,1-diphenyl-3,3-bis(p-methoxyphenyl)-1-butene (X). By a procedure similar to that employed for the oxidation of VII there was obtained a neutral and acidic fraction. The acidic fraction, 0.3 g. of a yellowish solid, m.p. 165–175°, was recrystallized from ethyl acetate and proved to be *p*-methoxybenzoic acid by its m.p., mixed m.p., and infrared spectrum.

When a similar oxidation was performed at 20°, only neutral materials were obtained.

Oxidation of 1,1-diphenyl-3,3-bis(p-methoxyphenyl)-1-butene (X). Through a solution of 1.0 g. (2.4 mmoles) of X in 100 ml. of ethyl acetate ozone was passed at −60° at a rate of 30 mg./min. After 5 min., 150 mg. (3.1 mmoles) was absorbed. The solvent was removed *in vacuo*, and the residue was treated with 50 ml. of formic acid and 1 g. of 50% hydrogen peroxide. The resulting mixture was heated 4 hr. at 70°, then refluxed for 15 min. and cooled. The solvent was evaporated *in vacuo*, and the residue was separated into neutral and acidic fractions by means of sodium bicarbonate. The neutral fraction amounted to 0.5 g. of a dark brown oil. The acidic fraction, 0.2 g. of a dark brown oil, could not be crystallized.

Oxidation of 3,3-bis(p-methoxyphenyl)-2-butanone (XII) *to the acid* V. 3,3-Bis(*p*-methoxyphenyl)-2-butanone was prepared by the method of Price and Mueller.[10] The ketone was then oxidized by the procedure of Voegtli and Lauger.[13] The crude yield was 5.0 g. (88.6%) of material melting at 86–95°. After recrystallization from ethanol the melting point was 104.5°. A qualitative test for chlorine was negative. The infrared spectrum was identical with the product obtained by methylation of Ia, and a mixture m.p. with this product showed no depression.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.48; H, 6.39; neut. equiv., 289.

Reaction of pyruvic acid and 2,2-bis(p-hydroxyphenyl)-propionic acid in concentrated sulfuric acid. Twenty-five and eight tenths grams (0.10 mole) of 2,2-bis(*p*-hydroxyphenyl)-propionic acid was added, over a period of 2–2.5 hr., to a mixture of 8.8 g. (0.10 mole) of pyruvic acid in 60 ml. of concd. sulfuric acid at −10°. The bright orange slurry was poured over crushed ice, and the resulting yellow precipitate was filtered, washed with water, and dried over concd. sulfuric acid. Trituration with a 1:1 mixture of ether and ethyl acetate to remove unchanged 2,2-bis(*p*-hydroxyphenyl)propionic acid gave 30.9 g. (94.0%). The product did not melt below 300°.

Anal. Found: Neut. equiv., 403.3; sapon. equiv., 154.3. The product was brominated as previously described. Bromine number, 715 and 695. Infrared maximum 1800 cm.$^{-1}$ (5-membered lactone).

Reaction of pyruvic acid and p-cresol in concentrated sulfuric acid. One hundred and eight grams (1.00 mole) of *p*-cresol was added, over a 3.5-hr. period, to a mixture of 44 g. (0.50 mole) of pyruvic acid in 300 ml. of concd. sulfuric acid at −10°. The product was isolated by addition of the reaction mixture to ice water, followed by washing with water and triturating with sodium bicarbonate solution. The product was finally washed with water and dried to give an amorphous solid. The yield was 63.1 g. (44.1% based on *p*-cresol). The product did not melt below 300°. Neut. equiv., 0; sapon. equiv. 199.7; mol. wt. (Rast), 1227. The infrared spectrum showed a strong 5-membered lactone band at 1800 cm.$^{-1}$ but no carboxyl carbonyl band at 1695 cm.$^{-1}$ The ferric chloride test for phenols was negative.

Reaction of pyruvic acid and anisole in concentrated sulfuric acid. One hundred and eight grams (1.0 mole) of anisole was added dropwise, over 2.25 hr., to a stirred solution of 44 g. (0.50 mole) of pyruvic acid in 300 ml. of concd. sulfuric acid at −10°. The mixture was allowed to react an additional 4 hr. The dark red solution was then poured over ice. The white precipitate was filtered, then dissolved in 10% sodium bicarbonate solution. After extraction with ether, the product was isolated by reprecipitation with concd. hydrochloric acid. The yield was 61.1 g. (42.7% based on anisole), melting point 205–210° dec.

Anal. Neut. equiv., 191.9; sapon. equiv., 0; mol. wt. (Rast), 1356. The infrared spectrum showed a strong car-

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(13) W. Voegtli and P. Lauger, *Helv. Chim. Acta*, **38**, 46 (1955).

boxyl carbonyl band at 1695 cm.$^{-1}$ but failed to show any lactone band.

2,2-Bis(3,5-dimethyl-4-hydroxyphenyl)propionic acid. The oil obtained from the reaction of 8.8 g. (0.1 mole) of pyruvic acid and 24.4 g. (0.2 mole) of 2,6-xylenol solidified on standing. The pink solid was dissolved in aqueous sodium bicarbonate. The resulting solution was washed with 50:50 ether–ethyl acetate and acidified with dilute hydrochloric acid. Filtration yielded 11.9 g. (38%) of white solid, m.p. 187–191° dec. Three recrystallizations of a 6-g. sample from 1,2-dichloroethane–acetone yielded 4.5 g. of white needles, m.p. 202–203° dec.

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05; neut. equiv., 314. Found: C, 72.50; H, 7.02; neut. equiv., 312.

3-Methyl-3-(2-hydroxy-5-methylphenyl)-5-methylcoumaran-2-one (XVI). A mixture of 86.4 g. (0.80 mole) of *p*-cresol and 17.6 g. (0.20 mole) of pyruvic acid in 150 ml. of glacial acetic acid was saturated with anhydrous hydrogen chloride and the contents of the flask stoppered and allowed to stand at room temperature for several days. At the end of the fifth day, the red solution was again saturated with anhydrous hydrogen chloride. After 9 days, the dark red solution was poured over crushed ice whereupon a light amber oil separated. The oily product was washed several times with water by decantation until the washings were neutral to litmus. The oil was then steam distilled to remove unchanged *p*-cresol. The resulting light tan colored oil thereupon solidified on standing overnight. The solid product was collected and dried *in vacuo* over sulfuric acid. The yield of crude product was 25.0 g. (46.6%) based on pyruvic acid. An analytical sample was obtained by three crystallizations from carbon tetrachloride, m.p. 83–84°, white prisms. Infrared maximum at 1790 cm.$^{-1}$ (5-membered lactone).

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.09; H, 6.01. Found: C, 76.05; H, 5.84.

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The Base-Catalyzed Conversion of Ketenes and Ketene Dimers to Ketene Trimers

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Dimethylketene and its dimer, tetramethyl-1,3-cyclobutanedione (IV), were converted by a base-catalyzed process to the trimer, hexamethyl-1,3,5-cyclohexanetrione (VII), which was hydrogenated over copper chromite to yield the *cis* and *trans* isomers of 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetriol. Diphenylketene gave the dimer, tetraphenyl-1,3-cyclobutanedione (VIII), and the trimer, hexaphenyl-1,3,5-cyclohexanetrione. The reaction of VIII with phenyllithium resulted in cleavage of the ring.

Ketoketenes dimerize upon standing or when heated to form substituted 1,3-cyclobutanediones. In some cases, depending upon the method employed for the preparation of the ketene, the product actually isolated is the ketene dimer. Thus, the dehydrohalogenation of isobutyryl chloride by the use of a tertiary amine leads to the dimer, tetramethyl-1,3-cyclobutanedione (IV),[1] but there is no evidence of symmetrical trimerization resulting in the formation of hexamethyl-1,3,5-cyclohexanetrione (VII), commonly known as hexamethylphloroglucinol.

The dimerization of ketoketenes is generally classified as a four-center-type reaction,[2] indicating that there are four atoms undergoing covalency change at the same time, and that evidence for the formation of ions or radicals as intermediates is lacking. Our experiments show, however, that ketoketenes, or their dimers may be converted rapidly and almost completely to their trimers in the presence of a basic catalyst such as sodium methoxide, thus suggesting that an ionic process may be involved. In this manner both dimethylketene and its dimer, tetramethyl-1,3-cyclobutanedione (IV), were converted to the dimethylketene trimer, hexamethyl-1,3,5-cyclohexanetrione (VII), a product obtained previously by Herzig and Erthal[3] by methylating phloroglucinol.

These results suggest a reaction mechanism that employs conventional ideas, and interprets these conversions as base-catalyzed, ionic processes which are reversible, thus accounting for the interconversion of ketene monomers, ketene dimers, and ketene trimers. It can be extended to account for even higher cyclic polymers. The methoxide ion catalyst attacks presumably the relatively positive carbonyl carbon atom of the ketene to form the enolate ion I. The next step in the reaction appears to be one between the ketene and the enolate ion I (similar to aldol addition) to form a second enolate ion II, which may either (a) undergo cycli-

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(1) E. Wedekind and W. Weisswange, *Ber.*, **39**, 1631 (1906).

(2) J. Hine, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, 1956, p. 453, *et seq.*

(3) J. Herzig and B. Erthal, *Monatsh.*, **32**, 505 (1911).