separated by filtration. They were still impure, m.p. 116–134°. This material was dissolved in boiling ether (80 ml. per gram of substance), and the solution was filtered while hot, and concentrated to one-fifth of its original volume. Crystallization was started by chilling. After 24 hours in the cold the crystals were filtered and dried in a vacuum at room temperature; m.p. 151–154°; *Anal.* Calc'd for I: Br, 11.83. Found: Br, 11.8.

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The Comparative Reactivities of *p*-Isopropylbenzoic Acid and Acetic Acid Toward the Methyl Free Radical

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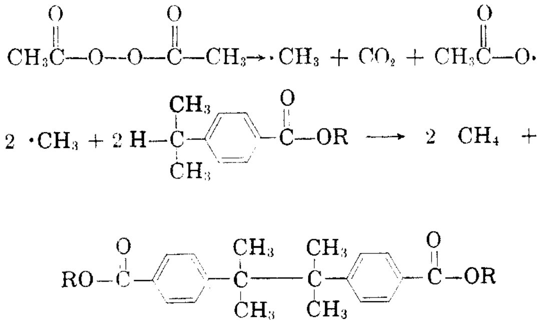
Previous studies[1] have indicated that the primary *beta* hydrogens in trimethylacetic acid are cleft by methyl free radicals with more difficulty (poorer yields) than are the *alpha* hydrogens in acetic acid. Preliminary studies made in our laboratories of reactions of methyl radicals in mixed solvents show that an equimolar mixture of isobutyric acid and isopropylbenzene reacts with the methyl free radical to produce the crossed dimer.[2] A crossed dimer is also obtained when an equimolar mixture of isopropylbenzene and methyl dichloroacetate is reacted with methyl free radicals.[2] These data suggest that the *tertiary alpha* hydrogens in isopropylbenzene, methyl dichloroacetate, and isobutyric acid are to a first approximation equally reactive toward hydrogen abstraction by methyl free radicals.

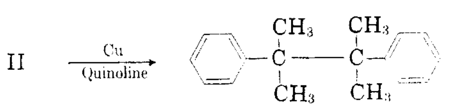
We have had need to synthesize 2,3-dimethyl-2,3-di-*p*-carboxyphenyl-*n*-butane. This synthesis has been accomplished by decomposing diacetyl peroxide in methyl *p*-isopropylbenzoate and subsequently saponifying the dimeric ester.



$$CH_3\overset{O}{\overset{\|}{C}}—O—O—\overset{O}{\overset{\|}{C}}—CH_3 \rightarrow \cdot CH_3 + CO_2 + CH_3\overset{O}{\overset{\|}{C}}—O\cdot$$

I, R = CH₃
II, R = H

This free unesterified dimeric acid (II) cannot be obtained directly from *p*-isopropylbenzoic acid, m.p. 113°, by this method without modification because the technique[3] requires that the solvent in which the diacetyl peroxide is decomposed must be a liquid at room temperature. We have overcome this difficulty by dissolving crystalline *p*-isopropylbenzoic acid in a mixture of acetic acid, acetic anhydride, and benzene. Thermal decomposition of diacetyl peroxide dissolved in this mixture produces pure 2,3-dimethyl-2,3-di-*p*-carboxyphenyl-*n*-butane. The methyl free radical attacks selectively from this mixture the *tertiary alpha* hydrogen from the *p*-isopropylbenzoic acid to give methane and the dimeric acid. This dimeric acid (II) and the dimeric ester (I) just described have by orthodox methods been converted each into the other. The structure of the dimeric acid (II) has been established by conversion to the well-known 2,3-dimethyl-2,3-diphenyl-*n*-butane through decarboxylation with copper powder in quinoline.[4]



These results demonstrate that the hydrogens in benzene, and more significantly, the *alpha* hydrogens in acetic acid are sufficiently more difficult to cleave with the methyl free radical than is the *alpha tertiary* hydrogen in *p*-isopropylbenzoic acid as to allow for complete selectivity in such a competitive system as is here described.

EXPERIMENTAL

Reagents. Eastman's white-label *p*-isopropylbenzoic acid, m.p. 112–114°, was used without further treatment. Methyl *p*-isopropylbenzoate was obtained through exhaustive esterification of this acid, b.p. 72°/0.5 mm., n_D^{20} 1.5113. The benzene was scrubbed with conc'd H_2SO_4 and doubly distilled from sodium. The acetic anhydride was Eastman's white-label product, and the acetic acid was Baker's C.P. grade. The preparation, isolation, analysis, and decomposition of the diacetyl peroxide in organic solvents has been described elsewhere.[3]

Thermal decomposition of diacetyl peroxide in methyl p-isopropylbenzoate. The preparation of 2,3-di-p-carbomethoxyphenyl-2,3-dimethyl-n-butane. A solution containing diacetyl peroxide, (14.2 g., 0.118 mole), dissolved in methyl *p*-isopropylbenzoate, (153.8 g., 0.80 mole), was introduced in single drops beneath the surface of methyl *p*-isopropylbenzoate, (79.0 g., 0.41 mole), held at 130°. The volatile products obtained and identified were carbon dioxide, (7.6 g., 0.17 mole), methane, (3.40 l., STP., 0.15 mole), and methyl acetate, (0.6 g., 0.009 mole), b.p., 54–56°. The material remaining in the reaction vessel was distilled at reduced pressure, and unreacted methyl *p*-isopropyl benzoate, (201.7 g., 1.0 mole), was collected at 76.5–79°/1 mm.; n_D^{20} 1.5082. The residual oil remaining in the distilling flask crystallized upon cooling to room temperature. These white crystals, (12.0 g.), were recrystallized from absolute methanol and melted at 210–211°.

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[1] Kharasch and Gladstone, *J. Am. Chem. Soc.*, **65**, 15 (1943); Kharasch, Jensen, and Urry, *J. Org. Chem.*, **10**, 386 (1945); Kharasch, Zimmerman, Zimmt, and Nudenberg, *J. Org. Chem.*, **18**, 1046 (1953); McBay and Tucker, *J. Org. Chem.*, **19**, 869 (1954).

[2] McBay, Unpublished results.

[3] Kharasch, McBay, and Urry, *J. Org. Chem.*, **10**, 394, 406 (1945).

[4] Shepard, Winslow, and Johnson, *J. Am. Chem. Soc.*, **52**, 2087 (1930).

Anal. Calc'd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.40. Found: C, 74.50; H, 7.49.

This ester upon saponification gave an acid identical with the one described in the following paragraph.

The reaction of diacetyl peroxide with p-isopropylbenzoic acid. The preparation of 2,3-di-p-carboxyphenyl-2,3-dimethyl-n-butane. The solvent used for this reaction had the following composition: acetic anhydride, 150.0 g., *p*-isopropylbenzoic acid, 237.0 g., acetic acid, 289.5 g., and benzene, 130.0 g. A solution containing diacetyl peroxide, 0.18 mole, dissolved in 587.0 g. of this mixed solvent was introduced one drop at the time beneath the surface of 182.5 g. of the same mixed solvent contained in a 3-liter flask (*see reference* 3) *and held at the reflux temperature,* 105°, of this mixture. The volatile products obtained and identified were carbon dioxide, (12.8 g., 0.30 mole), and methane, (4.74 l., STP., 0.21 mole). The unreacted solvent was removed from the residue in the reaction vessel by distillation at atmospheric pressure. A first fraction, (100.8 g.), b.p., 80–85°, was principally benzene. A section fraction, (450.2 g.), collected at 95–125°, was a mixture of benzene, acetic acid, and acetic anhydride. Upon cooling to room temperature the residue in the still-pot crystallized to a white solid. This white solid (crude dimeric acid, 22.8 g., 0.069 mole) was triturated with hot aqueous 50% ethanol and finally was recrystallized from a 5% solution of acetic acid in benzene, m.p. 275–280° with decomposition.

Anal. Calc'd for $C_{20}H_{22}O_4$: C, 73.62; H, 6.79; Neut. Equiv., 163. Found: C, 73.78; H, 6.89; Neut. Equiv., 163.

A sample of this dimeric acid, 2,3-di-*p*-carboxyphenyl-2,3-dimethyl-*n*-butane, (3.0 g.) was converted into the dimethyl ester, m.p. 212–213°. This ester did not depress the m.p. of the dimeric ester described in the previous paragraph.

The decarboxylation of 2,3-di-p-carboxyphenyl-2,3-dimethyl-n-butane. To a solution containing 3.35 g. of 2,3-di-*p*-carboxyphenyl-2,3-dimethyl-*n*-butane dissolved in 50 ml. of quinoline was added 1.0 g. of powdered copper, and this mixture was refluxed for 25–30 hours.[4] At intervals during this time there was added to the mixture in small samples a total of 1.0 g. of fresh copper powder. The mixture then was taken up in ethyl ether and was extracted repeatedly with 12 *M* HCl, then with H_2O, and finally with 5% NaOH followed by H_2O. After drying over $CaCl_2$, the neutral fraction was isolated by removing the ether on water-bath. The residue, 2.1 g., crystallized upon standing overnight. Recrystallization of this residue from 95% ethanol gave white crystals which melted at 113–114°. These crystals did not depress the m.p. (115°[5]), of authentic 2,3-dimethyl-2,3-diphenyl-*n*-butane. Attempts to decarboxylate the original dimeric acid (II) by fusion with soda-lime gave results that were much less satisfactory.

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[5] Klages, *Ber.*, **35**, 2638 (1902).

Betti Reactions of Some Phenols

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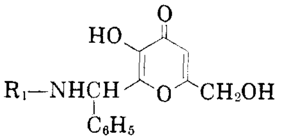
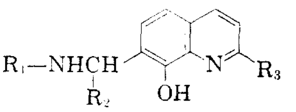
In continuation of previous work[1–3] on the preparation of chelating agents by the reaction of phenols with aromatic aldehydes and primary amines (Betti reaction)[4] some new derivatives of kojic acid, 8-quinolinol, and 8-hydroxyquinaldine have been obtained. Of these three phenols kojic acid is the most reactive; for example, it reacts with benzylideneaniline to precipitate the 6-substituted derivative (formula A) in less than one day at room temperature while 8-quinolinol requires weeks and 8-hydroxyquinaldine months for the corresponding reactions.

Betti reaction products from benzaldehyde and 8-hydroxyquinaldine, using aniline and ethyl anthranilate as the amines, were obtained in poor yields after long standing. On the basis of similarity of ultraviolet and infrared spectra of these two compounds to the spectra of the corresponding 8-quinolinol derivatives,[1] substitution was assumed to have occurred in the 7 position (formula B), although reaction at the active methyl group was a possibility since 8-hydroxyquinaldine is known to condense with benzaldehyde to yield 2-styryl-8-quinolinol.[5] Indeed, use of anthranilic acid as the amine gave a red product that may have resulted from the condensation of benzaldehyde with the active methyl group in addition to the expected Betti reaction; anthranilic acid was the only amine tried that could furnish the necessary acid catalysis for such a condensation. This red product was quite different from the other compounds prepared in this investigation and no further examination of it was made.



A



B

The chelating properties of 7-(α-anilinobenzyl)-8-hydroxyquinaldine and 7-[α-(*o*-carbethoxyanilino)benzyl]-8-hydroxyquinaldine (compounds V and VI in Table I) were unusual in that both compounds gave fluorescent yellow precipitates with aluminum ion in a neutral solution. All previously prepared 2-substituted 8-quinolinols have been characterized by failure to form an insoluble chelate compound with aluminum, presumably as a result of steric hindrance from the group in the 2 position.[6] The fact that the spectrum of the aluminum compound of VI is almost identical with the spectrum of VI itself rather than shifted to much longer wavelengths as is usual with the chelate compounds

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[1] Phillips, Keown, and Fernando, *J. Am. Chem. Soc.*, **75**, 4306 (1953).

[2] Phillips, Keown, and Fernando, *J. Org. Chem.*, **19**, 907 (1954).

[3] Phillips and Duckwall, *J. Am. Chem. Soc.*, **77**, 5504 (1955).

[4] Elderfield, *Heterocyclic Compounds*, John Wiley and Sons, New York, 1952, Vol. IV, p. 144.

[5] Phillips, Elbinger, and Merritt, *J. Am. Chem. Soc.*, **71**, 3986 (1949).

[6] Irving, Butler, and Ring, *J. Chem. Soc.*, 1489 (1949).