Condensation of Some Keto Esters with 2,4- and 2,6-Xylenols[1]

ROBERT V. SMITH AND MARK D. BEALOR

S. C. Johnson & Son, Inc., Racine, Wisconsin

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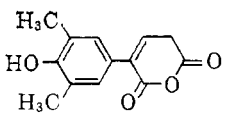
The condensation of several keto dibasic acid esters with 2,4- and 2,6-xylenols in cold concentrated sulfuric acid has been carried out. In the case of 2,6-xylenol, the corresponding bisphenol acids or esters were obtained with the exception of diethyl α-ketoglutarate, where two products were isolated, α-(3,5-dimethyl-4-hydroxyphenyl)glutaconic anhydride (I) and α,α-bis(3,5-dimethyl-4-hydroxyphenyl)glutaric anhydride (II). With 2,4-xylenol, several interesting lactone structures involving phenolic hydroxyl were formed. A spirodilactone was isolated from diethyl α-ketosuccinate. A nonspirodilactone, resulting from rearrangement, was formed from diethyl α-ketoglutarate. Structural assignments are based on elemental, infrared, and n.m.r. spectral analysis.

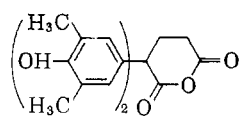
The reaction of α- and β-ketodicarboxylic acids with phenol was investigated. The products obtained were mixtures and difficult to purify. Infrared spectral analysis indicated that lactone structures, as well as the expected phenolic acids, were present indicating both *ortho* and *para* substitution had taken place.

The von Pechmann reaction for the preparation of coumarins from phenols and β-keto esters has been thoroughly reviewed.[2] Clayton[3] showed that 2,4-xylenol gave the expected 3,5,7-trimethylcoumarin when condensed with acetoacetic ester.

To minimize the formation of mixtures, 2,6-xylenol and 2,4-xylenol were condensed with the following keto acid esters: ketomalonate, ketosuccinate, α-ketoglutarate, β-ketoglutarate, and β-ketoadipate. 2,6-Xylenol gave the expected diphenolic acid or ester in each case with the exception of α-ketoglutarate which yielded two products, α-(3,5-dimethyl-4-hydroxyphenyl)glutaconic anhydride I and α,α-bis(3,5-dimethyl-4-hydroxyphenyl)glutaric anhydride II. The corresponding diethyl esters were prepared and characterized.



I

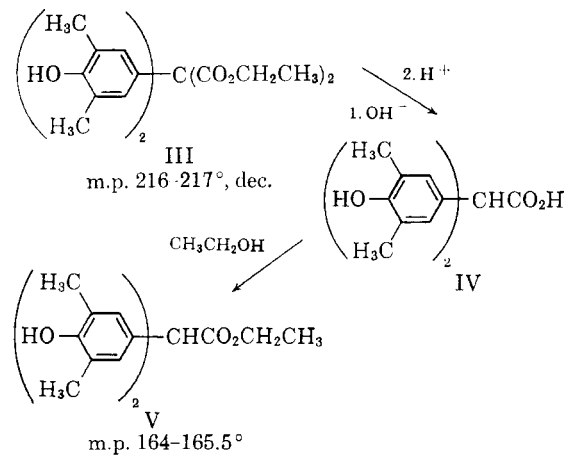


II

Diethyl bis(3,5-dimethyl-4-hydroxyphenyl)malonate III, the condensation product of diethyl ketomalonate and 2,6-xylenol, decarboxylated on hydrolysis with potassium hydroxide to yield bis-(3,5-dimethyl-4-hydroxyphenyl)acetic acid IV. The ethyl ester V was shown to be different from III.

The condensation products of 2,6-xylenol and the ketodicarboxylic esters are listed in Table I.

The infrared spectrum[4] of the product obtained

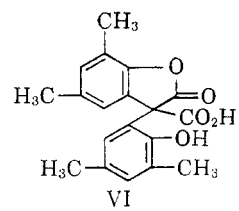


III
m.p. 216-217°, dec.

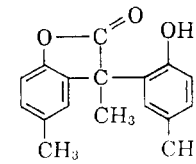
IV

V
m.p. 164-165.5°

from the reaction of diethyl ketomalonate and 2,4-xylenol shows a γ-lactone-carbonyl band at 1800 cm.$^{-1}$, a carboxyl carbonyl band at 1640 cm.$^{-1}$, and a hydroxyl band at 3570 cm.$^{-1}$. These data can be correlated with the 3-carboxy-3-(3,5-dimethyl-2-hydroxyphenyl) - 5,7 - dimethylcoumaran - 2 - one VI structure. Attempts to prepare the expected γ,γ-spirodilactone by treatment of VI with concentrated sulfuric acid or acetic anhydride were unsuccessful. An examination of the molecular model of the γ,γ-spirodilactone indicates a highly strained system would be present.



VI



VII

Smith *et al.*[5] have prepared 3-methyl-3-(2-hydroxy-5-methylphenyl)-5-methyl-coumaran-2-one VII and have shown that the lactone carbonyl absorption occurs at 1800 cm.$^{-1}$.

(1) Presented before the Division of Organic Chemistry, 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

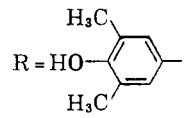
(2) S. Sethna and R. Phadke, *Org. Reactions*, **7**, 1 (1953).

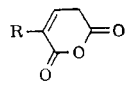
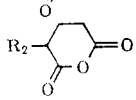
(3) A. Clayton, *J. Chem. Soc.*, 2016 (1908).

(4) Infrared spectra were determined on a Beckman IR-4 from solid films cast on a salt plate from acetone.

(5) Robert V. Smith, Chester L. Parris, Rostyslow Dowbenko, Norman A. Jacobson, John W. Pearce, and Roger M. Christenson, *J. Org. Chem.*, **27**, 455 (1962).

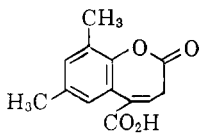
TABLE I



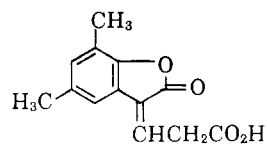
Ketone	Product	M.p., °C.	% Yield	Calcd. C	Calcd. H	Found C	Found H
Diethyl ketomalonate	$R_2C(CO_2CH_2CH_3)$	216–217, dec.	94	68.98	7.05	68.56	7.09
Diethyl ketosuccinate	$R_2C(CH_2CO_2H)(CO_2H)$	175–176	46	67.02	6.19	66.84	6.44
Dimethyl β-ketoglutarate	$R_2C(CH_2CO_2H)$	243–244, dec.	64	67.73	6.49	67.61	6.52
Diethyl α-ketoglutarate		225–225.5, dec.	22	67.73	5.20	67.21	5.29
Diethyl α-ketoglutarate		199–200	17	71.17	6.23	70.68	5.94
Diethyl β-ketoadipate[a]	$R_2C(CH_2CH_2CO_2H)(CH_2CO_2H)$	210–212	5	68.38	6.78	67.83	6.76

[a] Prepared according to the procedure of Riegel and W. M. Lilienfeld [*J. Am. Chem. Soc.*, 67, 1273 (1945)].

The reaction of diethyl α-ketoglutarate and 2,4-xylenol yielded two products. The infrared spectrum of one product had bands at 1740 cm.$^{-1}$ and 1670 cm.$^{-1}$. Condensation of one mole of 2,4-xylenol and lactonization could yield structures VIII or IX. The 1740-cm.$^{-1}$ band could be assigned to the ε-lactone in VIII or the α,β-unsaturate, γ-lactone carbonyl, in IX. The 1670-cm.$^{-1}$



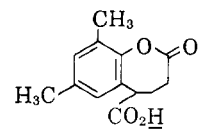
VIII



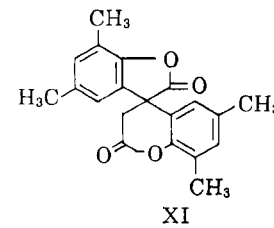
IX

band could be assigned to the α,β-unsaturated, carboxy carbonyl in VIII but not to the carboxy carbonyl in IX unless there is a shift of the double bond to conjugation with carboxyl carbonyl. Catalytic hydrogenation of this product yielded a saturated derivative with bands at 1740 cm.$^{-1}$ and 1720 cm.$^{-1}$. The lactone carbonyl band is still present at 1740 cm.$^{-1}$, and the carboxy carbonyl band has been shifted from 1670 to 1720 cm.$^{-1}$. The absence of a band at 1800 cm.$^{-1}$ in the saturated product is evidence that no γ-lactone structure is present. These data indicate that our 1:1 condensation product is VIII, α-(3,5-dimethyl-2-hydroxyphenyl)glutaconic acid, ε-lactone, and the hydrogenated product X the corresponding glutaric acid, ε-lactone.

The second product apparently resulted from the reaction of two moles of 2,4-xylenol with one mole of diethyl α-ketoglutarate followed by dilactonization. The infrared spectrum of this compound had

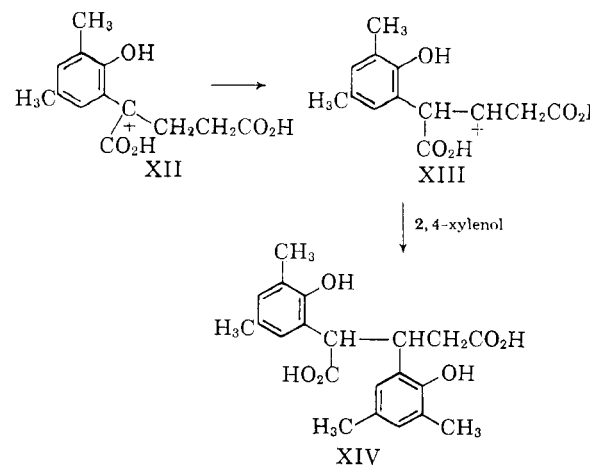


X



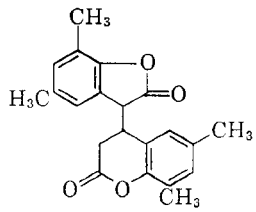
XI

bands at 1775 and 1800 cm.$^{-1}$. A possible structure is XI, the γ,ε-spirodilactone. The 1800-cm.$^{-1}$ band may be assigned to the γ-lactone carbonyl, but the ε-lactone carbonyl would be expected to absorb at a lower wave number than 1775 cm.$^{-1}$. If the intermediate carbonium ion XII rearranged to structure XIII which then alkylated a second mole of 2,4-xylenol, structure XIV would result. Of the two possible lactones, XV and XVI, resulting from

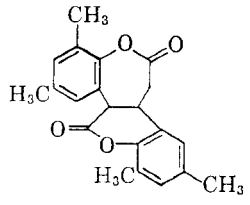


XII XIII XIV

cyclization of XIV, the former is in accord with spectral evidence for the presence of both a γ-lactone (1800 cm.$^{-1}$) and a δ-lactone (1775 cm.$^{-1}$) carbonyl.

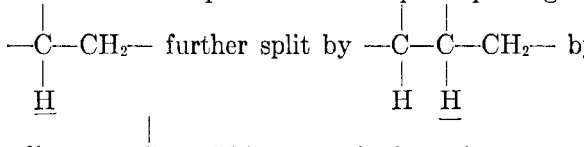


XV

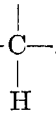


XVI

Structure XV is also preferred based on n.m.r. spectral analysis. A doublet corresponding to —CH$_2$—CH— and not the splittings expected of —CH$_2$—CH$_2$— is assigned. Also, a sextet is present which corresponds to the triplet splitting of

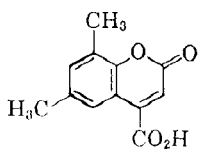


adjacent

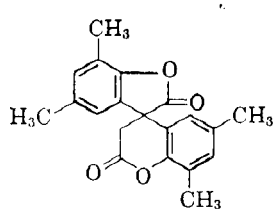


. This system is absent in structure XI.

Two products were isolated from the reaction of diethyl ketosuccinate and 2,4-xylenol. One of the products is postulated as 4-carboxy-6,8-dimethylcoumarin XVII. The infrared spectrum has a band at 1720 cm.$^{-1}$ which is assigned to the α,β-unsaturated, δ-lactone carbonyl and a band at 1680 cm.$^{-1}$ which is assigned to the α,β-unsaturated, carboxyl carbonyl. The infrared spectrum of coumarin was determined and shown to have a lactone carbonyl band at 1720 cm.$^{-1}$.



XVII

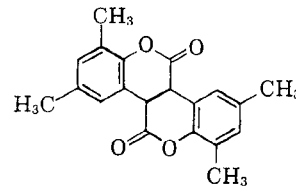


XVIII

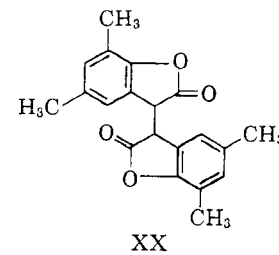
Reaction of two moles of 2,4-xylenol with one mole of diethyl ketosuccinate and dilactonization yielded the second product. A possible structure is the γ,δ-spirodilactone XVIII. The infrared spectrum of this compound had a band at 1800 cm.$^{-1}$, assigned to the γ-lactone carbonyl and one at 1775 cm.$^{-1}$ which is assigned to the δ-lactone carbonyl.

Structures XIX and XX would result if rearrangement preceded alkylation and cyclization as previously described for the formation of compound XV.

Structure XIX, however, would have only a δ-lactone carbonyl band and XX only a γ-lactone carbonyl band. Based on this evidence XVIII,



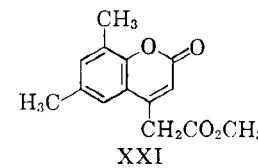
XIX



XX

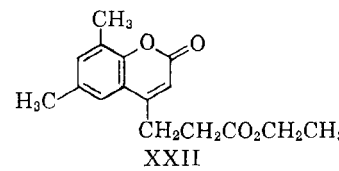
spiro(6,8-dimethyldihydrocoumarin)-4,3′-(5′,7′-dimethylcoumaran-2′-one) is postulated as the structure for the product from two moles of 2,4-xylenol and one mole of diethyl ketosuccinate.

With dimethyl β-ketoglutarate, condensation of one mole of 2,4-xylenol and lactonization yielded the methyl ester of 6,8-dimethylcoumarin-4-acetic acid XXI in 83% yield and the corresponding free acid in 10% yield. Under the conditions used, concentrated sulfuric acid at 0°, the von Pechmann reaction product was isolated almost quantitatively.



XXI

From the reaction of diethyl β-ketoadipate and 2,4-xylenol only the normal von Pechmann product XXII was isolated.



XXII

Experimental

General Procedure for the Condensation of Keto Ester and Xylenol.—To 60 ml. of concentrated sulfuric acid (*d* 1.84) maintained at 0–5° was added the keto ester (0.1 mole). While maintaining the mixture at this temperature and with stirring, the xylenol (0.2 mole) was added. The resulting mixture was then stirred at this temperature an additional 6 hr. On pouring the highly colored, reaction mixture into 500 g. of ice water the product separated as an oil. The purification procedure for each reaction is given in detail under the specific headings below.

3-Carboxy-3-(3,5-dimethyl-2-hydroxyphenyl)-5,7-dimethylcoumaran-2-one (VI).—The oil obtained from the reaction of 17.4 g. of diethyl ketomalonate (0.1 mole) and 24.4 g. of 2,4-xylenol (0.2 mole) solidified on standing and was collected. Trituration with aqueous sodium bicarbonate and collection yielded 18.6 g. (57%); m.p. 163–172° dec. Recrystallization from nitromethane yielded 6 g. of pink needles, m.p. 257–261° dec. An analytical sample was obtained after two additional recrystallizations from 1,2-dichloroethane, m.p. 266–269° dec.

All microanalyses were carried out by Micro-Tech Laboratories, 8000 Lincoln Ave., Skokie, Illinois. All boiling and melting points are uncorrected.

Anal. Calcd. for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found: C, 70.51; H, 5.13.

Diethyl Bis(3,5-dimethyl-4-hydroxyphenyl)malonate (III).—The oil obtained from the reaction of 17.4 g. of diethyl malonate (0.1 mole) and 24.4 g. of 2,6-xylenol (0.2 mole) solidified on standing and was collected, yield 37.5 g.; (94%), m.p. 182–185° dec. Recrystallization from nitromethane gave 17.5 g. of pink needles, m.p. 211.5–213° dec. An analytical sample was obtained after three additional recrystallizations from nitromethane, m.p. 216–217° dec.

Anal. Calcd. for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 68.56; H, 7.09.

Bis(3,5-dimethyl-4-hydroxyphenyl)acetic Acid (IV).—A mixture of 10 g. of diethyl bis(3,5-dimethyl-4-hydroxyphenyl)malonate (0.025 mole), 20 g. of potassium hydroxide (0.35 mole), 60 ml. of water, and 20 ml. of ethanol was refluxed for 16 hr. The hot solution was treated with decolorizing charcoal, filtered, and acidified with dilute hydrochloric acid. Filtration yielded 7.5 g. (100%) of solid. Three recrystallizations from ethanol–water yielded 5 g. of tan plates, m.p. 208–210° dec.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71; Neut. Equiv., 300. Found: C, 72.10; H, 6.64; Neut. Equiv., 301.

Ethyl Bis(3,5-dimethyl-4-hydroxyphenyl)acetate (V).—A solution of 8.5 g. of bis(3,5-dimethyl-4-hydroxyphenyl) acetic acid (0.0283 mole) in 50 ml. of absolute ethanol was saturated with dry hydrogen chloride and refluxed for 20 hr. After cooling 9 g. (97.5%) of crystalline solid was collected, m.p. 161–163.5°. Three recrystallizations from benzene yielded 5 g. of tan needles, m.p. 164–165.5° dec.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 73.04; H, 7.22.

α,α-Bis(3,5-dimethyl-4-hydroxyphenyl)succinic Acid.—The oil obtained from the reaction of 21 g. of diethyl oxalacetate sodium salt (0.1 mole) and 24.4 g. of 2,6-xylenol (0.2 mole) solidified on standing and was collected, yield 19 g. (46%); m.p. 115–120°. The crude solid was steam distilled and the residue refluxed for 16 hr. with 40 g. of potassium hydroxide (0.71 mole), 120 ml. of water, and 40 ml. of ethanol. The hot solution was treated with decolorizing charcoal, filtered, and acidified with dilute hydrochloric acid. Filtration yielded 13.6 g. (38%) of white solid, m.p. 135–140°. Recrystallization from 80 ml. of nitromethane gave 12.6 g. of white plates, m.p. 168–173°. An analytical sample was obtained after four additional recrystallizations from nitromethane, m.p. 175–176°.

Anal. Calcd. for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19; neut. equiv., 179. Found: C, 66.84; H, 6.44; neut. equiv., 180.

Spiro[(6,8-dimethyldihydrocoumarin)-4,3′-(5′,7′-dimethylcoumaran-2′-one] (XVIII).—The oil obtained from the reaction of 21 g. of diethyl oxalacetate sodium salt (0.1 mole) and 24.4 g. of 2,4-xylenol (0.2 mole) partially solidified on standing and was collected, yield 26 g. The crude solid was steam distilled and the residue refluxed for 16 hr. with 40 g. of potassium hydroxide, (0.71 mole), 120 ml. of water, and 40 ml. of ethanol. The hot solution was treated with decolorizing carbon, filtered, and cooled. Filtration yielded 14.5 g. (28.4%) of white needles, m.p. > 300°.

Anal. Calcd. for $C_{20}H_{18}O_6K_4$: C, 47.03; H, 3.55. Found: C, 48.23; H, 4.77.

The analytical data indicate the product is the impure **tetrapotassium salt of α,α-bis(3,5-dimethyl-2-hydroxyphenylsuccinic acid.**

A sample of this salt, 8.5 g., dissolved in 100 ml. of water and acidified with dilute hydrochloric acid yielded 5 g. of (XIX), m.p. 143–145°. This on recrystallization from ethanol–water and then from methylcyclohexane yielded 1.33 g. of white needles, m.p. 165.5–166.5°.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.34; H, 5.63.

The filtrate from the tetrapotassium salt of α,α-bis(3,5-dimethyl-2-hydroxyphenyl)succinic acid on acidification with dilute hydrochloric acid yielded 9.5 g. (29.4%) of **4-carboxy-6,8-dimethylcoumarin** (XVII), m.p. 235–240° dec. Three recrystallizations from nitromethane–methanol yielded 3.5 g. of yellow needles, m.p. 245–246° dec.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62; neut. equiv., 218. Found: C, 66.09; H, 4.80; neut. equiv., 216.

β,β-Bis(3,5-dimethyl-4-hydroxyphenyl)glutaric Acid.—The oil obtained from the reaction of 17.4 g. of dimethyl β-ketoglutarate (0.1 mole) and 24.4 g. of 2,6-xylenol (0.2 mole) solidified on standing. Trituration with aqueous sodium bicarbonate and collection yielded 32. g. (80%). A portion, 10 g., of this product (0.025 mole) was refluxed for 16 hr. with 20 g. of potassium hydroxide, (0.35 mole), 60 ml. of water, and 20 ml. of ethanol. The hot solution was treated with decolorizing charcoal, filtered, and acidified with dilute hydrochloric acid. Filtration yielded 7.5 g. (81%) of tan solid, m.p. 234–236° dec. Four recrystallizations from nitroethane–methanol yielded 4.5 g. of white needles, m.p. 243–244° dec.

Anal. Calcd. for $C_{21}H_{24}O_6$: C, 67.73; H, 6.49; neut. equiv., 186. Found: C, 67.61; H, 6.52; neut. equiv., 185.

4-Carbomethoxymethyl-6,8-dimethylcoumarin (XXI).—The oil obtained from the reaction of 17.4 g. of dimethyl β-ketoglutarate (0.1 mole) and 24.4 g. of 2,4-xylenol yielded 23.5 g. of solid on standing. The crude product was continuously extracted with 700 ml. of methylcyclohexane for 10 hr. The extract deposited 19 g. (77%) of white needles on cooling, m.p. 110–11°. After three additional recrystallizations, 8 g. yielded 6 g., m.p. 112.5–113°.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 67.98; H, 5.69.

The methylcyclohexane-insoluble fraction on recrystallization from nitromethane–methanol yielded 2.5 g. (10.8%) of **4-carboxymethyl-6,8-dimethylcoumarin**, m.p. 162–164° dec. Three additional recrystallizations yielded white needles, m.p. 212–213° dec.

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21; neut. equiv., 232. Found: C, 67.16; H, 5.38; neut. equiv. 233.

α-(3,5-Dimethyl-4-hydroxyphenyl)glutaconic Anhydride (I).—The oil which separated from the reaction of 20.2 g. of diethyl α-ketoglutarate (0.1 mole) and 24.4 g. of 2,6-xylenol solidified on standing and was collected, yield 22.3 g., m.p. 96–99° dec. Recrystallization from 1,2-dichloroethane yielded 4.8 g. (22.2%) of I, m.p. 225–227° dec. Three recrystallizations from nitromethane yielded yellow needles, m.p. 225–225.5° dec.

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.63; H, 5.20. Found: C, 67.21; H, 5.29.

The 1,2-dichloroethane filtrate from I yielded 6.1 g. (17.2 %) of **α,α-bis(3,5-dimethyl-4-hydroxyphenyl)glutaric anhydride** (II), m.p. 188.5–191.5°. Three recrystallizations from 1,2-dichloroethane-methylcyclohexane yielded white granules, m.p. 199–200°.

Anal. Calcd. for $C_{21}H_{22}O_5$: C, 71.17; H, 6.23. Found: C, 70.68, H, 5.94.

Diethyl α,α-Bis(3,5-dimethyl-4-hydroxyphenyl)glutarate.—A solution of 4.1 g. of α,α-bis(3,5-dimethyl-4-hydroxyphenyl)glutaric anhydride (0.0116 mole) in 50 ml. of absolute ethanol was saturated with dry hydrogen chloride and refluxed for 16 hr. On pouring into 500 ml. of ice water an oil separated and slowly solidified, yield 3 g. (60.5%); m.p. 143–144° dec. Three recrystallizations from nitromethane yielded white granules, m.p. 156–158°.

Anal. Calcd. for $C_{25}H_{32}O_6$: C, 70.07; H, 7.53. Found: C, 69.82; H, 7.38.

Diethyl α-(3,5-Dimethyl-4-hydroxyphenyl)glutaconate.—A solution of 3.18 g. of α-(3,5-dimethyl-4-hydroxyphenyl)-glutaconic anhydride (0.0137 mole) in 150 ml. of absolute ethanol was saturated with dry hydrogen chloride and refluxed for 19 hr. On cooling 0.84 g. of unchanged anhydride was recovered. Dilution of the filtrate with 225 ml. of water and cooling yielded 2 g. (66%) of solid, m.p. 83–84°. Recrystallization from methylcyclohexane yielded 1.7 g., m.p. 81–82°. Two additional recrystallizations yielded white rods, m.p. 85–86°.

Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.66; H, 7.24. Found: C, 66.69; H, 7.56.

α-(3,5-Dimethyl-2-hydroxyphenyl)glutaconic Acid, ε-Lactone (VIII).—The solid obtained from the reaction of 20.2 g. of diethyl α-ketoglutarate (0.1 mole) and 24.4 g. of 2,4-xylenol (0.2 mole) was collected and dried, yield 21.6 g. This was steam distilled and the residue refluxed for 16 hr. with 40 g. of potassium hydroxide (0.71 mole), 120 ml. of water, and 40 ml. of ethanol. The hot solution was treated with decolorizing charcoal, filtered, and acidified with dilute hydrochloric acid. Filtration yielded 21.6 g. of yellow solid. Recrystallization from 150 ml. of nitromethane yielded 3.5 g. (15%) of white microcrystalline product, m.p. 240–244° dec. An analytical sample was obtained after two additional crystallizations from nitromethane, m.p. 245–246.5° dec.

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.23; H, 5.20. Found: C, 67.28; H, 5.31.

The nitromethane mother liquor from VIII was stripped at reduced pressure and 60° and the residue continuously extracted with 225 ml. of methylcyclohexane for 12 hr. Evaporation of the solvent left a residue which was taken up in 22.4 g. of potassium hydroxide (0.4 mole), and 150 ml. of water. Acidification and filtration yielded 7.6 g. (22.5%) of yellow solid, m.p. 105–108°. Recrystallization from glacial acetic acid–water gave 4.5 g. of **3-[4-(6,8-dimethyldihydrocoumaryl)]-5,7-dimethylcoumaran-2-one (XV)**, m.p. 129–131°. An analytical sample was obtained after two recrystallizations from methylcyclohexane; m.p. 148–150°.

Anal. Calcd. for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 75.10; H, 6.18.

α-(3,5-Dimethyl-2-hydroxyphenyl)glutaric Acid, ε-Lactone (X).—Two grams of α-(3,5-dimethyl-2-hydroxyphenyl)glutaconic acid, ε-lactone (0.0086 mole), 0.1 g. of platinum oxide, and 25 ml. of glacial acetic acid were shaken at room temperature for 2 hr. under an initial hydrogen pressure of 35 p.s.i., after which time hydrogenation was complete. On pouring into ice water 1.7 g. (85%) of white solid, m.p. 165–168°, precipitated. An analytical sample was obtained after two recrystallizations from nitromethane; white needles, m.p. 168–169.5°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.66, H, 6.02. Found: C, 66.55; H, 5.94.

β,β-Bis(3,5-dimethyl-4-hydroxyphenyl)adipic Acid.—The crude product obtained from the reaction of 33.5 g. of diethyl β-ketoadipate (0.155 mole) and 37.8 g. of 2,6-xylenol (0.31 mole) was steam distilled and refluxed for 16 hr. with 40 g. of potassium hydroxide (0.71 mole), 120 ml. of water, and 40 ml. of ethanol. Acidification with dilute hydrochloric acid and filtration yielded 9 g. of tan solid. Trituration with hot 1,2-dichloroethane left 3 g. (5%) of residue; m.p. 189.5–195° dec. An analytical sample was obtained after four recrystallizations from nitromethane; white needles, m.p. 210–212° dec.

Anal. Calcd. for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78. Found: C, 67.83; H, 6.76.

4-(2-Carbethoxyethyl)-6,8-dimethylcoumarin (XXII).—The oil obtained from the reaction of 19 g. of diethyl β-ketoadipate (0.088 mole) and 21.5 g. of 2,4-xylenol (0.176 mole) solidified on standing and was collected, yield 4.6 g. (19%); m.p. 82–84°. Four recrystallizations from methylcyclohexane–methanol yielded 2 g. of white needles, m.p. 85–85.5°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.94; H, 6.46.

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The Mechanism of Formation of the Sodium Salt of Tetraethylpropene-1,1,3,3-tetracarboxylate during the Reaction of Dichlorocarbene with the Sodium Salt of Diethyl Malonate

A. P. KRAPCHO, P. S. HUYFFER,[1] AND I. STARER[2]

Department of Chemistry, University of Vermont, Burlington, Vermont

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The reaction of dichlorocarbene with the sodium salt of diethyl malonate (I) has been shown to lead to the formation of the sodium salt of tetraethylpropene-1,1,3,3-tetracarboxylate (II). A plausible mechanistic route leading to formation of II is presented and discussed.

The reaction of the sodium salt of diethyl malonate (I) with chloroform in the presence of sodium ethoxide has been reported to yield the sodium salt of tetraethylpropene-1,1-3,3-tetracarboxylate (II).[3] Since Hine[4] has clearly demonstrated that the basic hydrolysis of chloroform proceeds *via* dichlorocarbene, it seemed probable that II was formed from reaction with a carbene precursor. In order to elucidate the mechanism of formation of II, a study of this reaction was performed.

$$\underset{\text{I}}{Na^+\bar{C}H(CO_2Et)_2} \qquad \underset{\text{II}}{(EtO_2C)_2\bar{C}—CH{=}C(CO_2Et)_2Na^+}$$

To obtain evidence for the possible intermediacy of dichlorocarbene, the sodium salt of diethyl malonate (I) was prepared in dry 1,2-dimethoxyethane and to this solution sodium trichloroacetate was added in approximately a 2:1 molar ratio. The resulting solution was refluxed for one hour,

(1) NDEA Fellow.

(2) American Cyanamid Company, Bound Brook, New Jersey.

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