one hour. The pale brown solution was then poured into cold dilute hydrochloric acid. On standing the product solidified in faintly purple needles. It weighed 0.83 g. (86%) and was soluble in alkali. The material had a phenolic odor and showed a characteristic tendency to sublime, filling the tube in which it was stored with a dense mass of fine needles (m. p. 43–45°).

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.92; H, 8.55. Found: C, 82.86; H, 8.74.

5-Alloxy-4,7-dimethylhydrindene (allyl ether of II).—A mixture of 2.2 g. of 5-hydroxy-4,7-dimethylhydrindene (II) 2.2 g. of finely powdered anhydrous potassium carbonate and 1.8 g. of allyl bromide in 35 cc. of methyl ethyl ketone was refluxed for twenty-four hours. The product was a colorless oil distilling at 107–108° at 2 mm. The yield was nearly quantitative.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.14; H, 8.95. Found: 3, 83.20; H, 8.70.

5 - Hydroxy - 6 - allyl - 4,7 - dimethylhydrindene (IV).—When a mixture of 1.34 g. of the above allyl ether and 3.00 g. of dimethylaniline was heated to 280° in a sealed tube and the amine was removed by dilute hydrochloric acid, the product was obtained in 75% yield as a pink solid. The color was removed by two crystallizations from petroleum ether but always returned on standing in contact with air. A sample stored in the ordinary way turned a bright violet in the course of two months while one kept in a sealed tube showed no color change. The melting point remained unaffected, however, at 66–67°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.14; H, 8.95. Found: C, 83.38; H, 8.94.

Summary

The diazo coupling of and the rearrangement of the allyl ethers of 5-hydroxy-6-methylhydrindene and 5-hydroxy-4,7-dimethylhydrindene have been investigated with results which concur with much other evidence that the Mills–Nixon effect is at the most qualitative in the case of hydrindene.

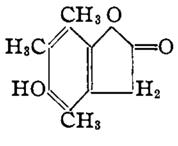
HARTFORD, CONNECTICUT RECEIVED OCTOBER 13, 1939

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

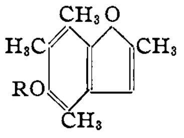
The Reaction between Quinones and Metallic Enolates. X. Trimethylquinone and the Enolates of β-Diketones[1]

BY LEE IRVIN SMITH AND E. W. KAISER[2]

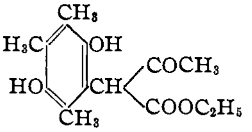
A few years ago, Smith and MacMullen[3] added the enolates of malonic ester and acetoacetic ester to trimethylquinone. From the malonic ester addition, one product, the isocoumaranone I, was obtained, while the addition of acetoacetic ester led to two substances, the isocoumaranone I, and the coumaron II. The formation of these products was interpreted as a primary 1,4-addition of the enolate to the quinone conjugated system which carried no substituent in the β-position, to give III (from acetoacetic ester), followed by the usual cleavages and ring closure.



I

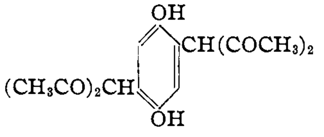


II, R = H
IX, R = Ac

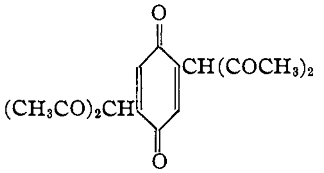


III

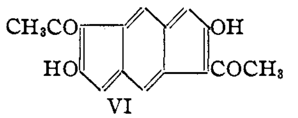
Ionescu[4] studied the reaction between acetylacetone and *p*-benzoquinone. The reaction was interpreted as an initial 1,4-addition of the β-diketone (two molecules), leading first to IV (not isolated) which was then oxidized by excess quinone or by air to V (also not isolated). The latter



IV



V



VI

---

(1) Paper IX, *J. Org. Chem.*, **4**, 342 (1939).

(2) Abstracted from a thesis by E. W. Kaiser, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, August, 1939.

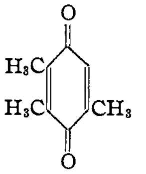
(3) THIS JOURNAL, **58**, 629 (1936).

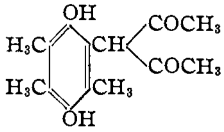
(4) Ionescu, *Bull. soc. chim.*, **37**, 913 (1925); **41**, 1094 (1927); **51**, 171 (1932).

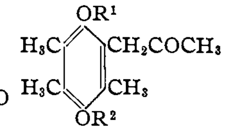
substance then underwent ring closure by elimination of water between the quinone oxygen atoms and a methyl group in each of the side chains, to give the final product, which was represented as VI. This substance VI is essentially a methylenequinone, and its formation from IV or V by ring closure involving a break in the carbon–oxygen bond of the quinone V or hydroquinone IV represents a rather unusual type of reaction.

In order to study this reaction, as well as to extend the general study of the addition of enolates to quinones, we have investigated the addition of the enolates of two β-diketones (acetylacetone and acetylisobutyrylmethane) to trimethylquinone VII. This quinone was chosen because it has but one open position, and previous work[3] had indicated that only one molecule of enolate would add to a quinone substituted in this manner. Moreover, since the first reaction products would be substances of the type of III, it seemed possible that this reaction might serve as a useful method for preparation of a variety of 5-hydroxycoumarons, which would be useful as sources of model compounds for use in investigations of certain phases of the chemistry of vitamin E.

When a dilute alcoholic solution of the quinone VII was added slowly to the enolate of acetylacetone, the product, formed in 72% yield, was the phenylacetyl acetone VIII. This substance reacted with phenylhydrazine, and was readily converted into the known coumarone II by action of hot concentrated hydrochloric acid.

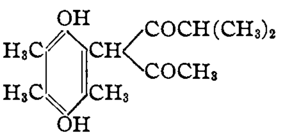

VII

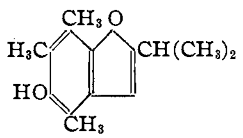

VIII

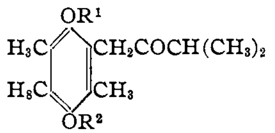

X, $R^1 = R^2 = Ac$
XI, monoxime of X
XIV, $R^1 = (CH_3)_2CHCO$; $R^2 = Ac$
XV, monoxime of XIV
XVII, $R^1 = Ac$; $R^2 = (CH_3)_2CHCO$
XVIII, $R^1 = Ac$; $R^2 = CH_2ClCO$

The action of acetic anhydride containing a trace of sulfuric acid upon the diketone VIII resulted in acetylation of both hydroxyl groups and the simultaneous loss of one of the acetyl groups from the β-diketone residue. The product X formed a monoxime XI, gave a negative phenol test (Folin), and was transformed by hot concentrated hydrochloric acid into the coumaron II. Attempts were made to hydrolyze the acetate X to the dihydroxy compound, using dilute sodium hydroxide, but this reagent also transformed X into the coumaron II, even at room temperature. Dilute hydrochloric acid under varying conditions either did not attack the acetate X, or else transformed it into the coumaron. From these results, and analogy with previous work,[3] there appears to be little doubt concerning structure VIII for the primary product of the reaction.

When the enolate of acetylisobutyrylmethane was added to the quinone VII, the product, formed in 81% yield, was the phenylated diketone XII. This substance reacted with phenylhydrazine, and was converted by action of hydrochloric acid into a mixture of coumarons, II and XIII, although the pure compounds were not separated from this mixture. Acetylation of XII with acetic anhydride containing a trace of sulfuric acid produced a mixture, from which a substance having the composition $C_{18}H_{24}O_5$ was isolated. This substance formed a monoxime XV, and in analogy with the acetylation of VIII, it was at first thought that the substance was the diacetoxybenzyl isopropyl ketone, XVI. However, when it was discovered that the action of hot hydrochloric acid upon $C_{18}H_{24}O_5$ produced the coumaron II, it became obvious that this compound could not possess the side chain of XVI, but must contain the acetone side chain of X, since XVI, on cyclization, would produce the coumaron XIII. Since $C_{18}H_{24}O_5$ gave a negative phenol test, and since it was isomeric with XVI, only two formulas for it were possible: XIV and XVII.


XII

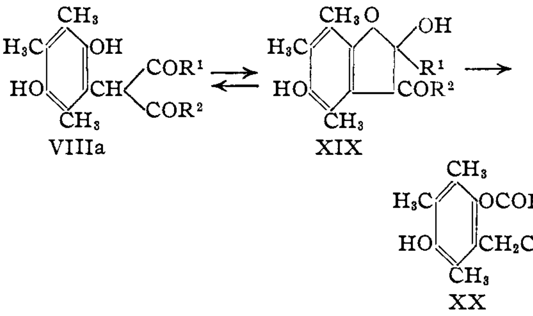

XIII


XVI, $R^1 = R^2 = Ac$

The choice between XIV and XVII was made as follows: the diketone VIII from acetylacetone was acylated with isobutyric anhydride. The product, XVII, formed in 56% yield, was a new substance also having the composition $C_{18}H_{24}O_5$. This substance also gave a negative phenol test. When VIII was acylated with chloroacetic anhydride a product XVIII resulted which contained only one chloroacetyl group. It followed, therefore, that when substances of the type of VIII and XII were acetylated, the reaction involved a migration of one of the acyl groups from the diketone side chain to the *ortho* oxygen atom, and simultaneous acylation of the other hydroxyl group by the acylating agent used. On this basis, the first substance was assigned structure XIV, while its isomer, obtained from isobutyric anhydride and VIII, was assigned structure XVII. It followed also that the chloroacetyl derivative XVIII had an analogous structure; that is, an acetyl group of VIII migrated from the side chain to the *ortho*-oxygen atom, and simultaneously the other hydroxyl group was chloroacetylated.

That the reaction is a true intramolecular rearrangement is indicated by the yields of the products obtained in these acylations. If the reaction involved a complete rupture of an acyl group from the molecule, this acyl group would then be present in the reaction mixture as an acid, a simple anhydride, or a mixed anhydride, together with a large excess of the acylating agent used. Under these circumstances, *acetylation* of XII could give rise to no less than seven different compounds. Unless the isobutyryl group had a *much* greater acylating power than any of the other possible acyl groups, it could not have left the molecule entirely and then reëntered at some other position to give over 30% of XIV in the presence of a large excess of acetic anhydride. The fact that cleavage of the mixed β-diketone XII could occur in more than one way renders the probability of isolating XIV in good yield even less likely, assuming a mechanism which involved cleavage. Moreover, chloroacetic anhydride is much more reactive toward the hydroxyl group than is acetic anhydride, while isobutyric anhydride is the least reactive of the three in this respect.[5] Therefore, if in the acylation of VIII with either chloroacetic anhydride or isobutyric anhydride, the cleavage of an acetyl group had occurred to give acetic anhydride, competing reactions would have resulted in the formation of acylation products containing two chloroacetoxy groups in one case and two acetoxy groups in the other. Actually, however, the acylating agent used supplies only one acyl group; the other acetoxy group is derived from one of the acyl groups in the β-diketone side chain.

These results can be explained by assuming a primary ring closure between one carbonyl group of the β-diketone VIIIa and the *ortho* hydroxyl group to give a hemiacetal, XIX. This intermediate, being a potential β-diketone, can be cleaved to give the final product, a phenolic ester XX



This cleavage is analogous to the well-known decarboxylation of certain β-hydroxy acids which occurs on dehydration, and also to the cleavage of the addition products of certain β-diketones and Grignard reagents, observed by Kohler and Erickson.[6]

In these rearrangements, there is involved the shift of an acyl group from carbon to oxygen. Such rearrangements are very unusual, the reverse shift, from oxygen to carbon, being the common type. Nevertheless, a few examples of this sort have been recorded. Thus Kohler and Erickson[6] found that addition of one mole of phenylmagnesium bromide to diphenyl triketone XXI produced not the expected phenyldibenzoylcarbinol XXII but the benzoate of benzoin XXIII. Likewise, Blatt and Hawkins[7] reported that dibenzoylcarbinol XXIV, when vacuum distilled, rearranged to the benzoate of benzoylcarbinol XXV.

$C_6H_5COCOCOC_6H_5$ XXI

$(C_6H_5CO)_2C(OH)C_6H_5$ XXII

$C_6H_5COCH(C_6H_5)OCOC_6H_5$ XXIII

$C_6H_5COCHOHCOC_6H_5$ XXIV

$C_6H_5COCH_2OCOC_6H_5$ XXV

Attempts were made to add *n*-butyrylacetylmethane, benzoylacetone, and dibenzoylmethane to trimethylquinone, without success. Addition of the first of these diketones led to an oil, which could not be crystallized; addition of benzoylacetone produced only a very small amount of tan solid; while the only product obtained when dibenzoylmethane was used was unchanged diketone.

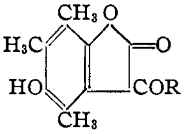
---

[5] Wilson and Sidgwick, *J. Chem. Soc.*, **103**, 1959 (1913).

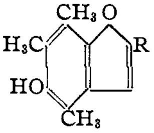
[6] Kohler and Erickson, THIS JOURNAL, **53**, 2305 (1931).

[7] Blatt and Hawkins, *ibid.*, **58**, 81 (1936).

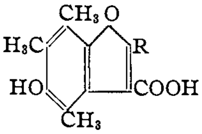
The method of Smith and MacMullen has been used by Bergel, Jacob, Todd and Work[8] for the preparation of coumaron and coumaran derivatives; from the product of addition of acetoacetic esters to trimethylquinone, these authors isolated three substances, the acyl isocoumaranone XXVI (main product), the coumaron XXVII, and the coumaron carboxylic acid XXVIII (R = $C_{15}H_{31}$ and $C_{17}H_{35}$).



XXVI



XXVII



XXVIII

Karrer, Escher and Rentschler[9] have also used the method; by addition of propionylacetic ester to the quinone they obtained the coumaron XXVIII (R = C_2H_5).

Repetition of the experiment of Smith and MacMullen[3] under slightly different conditions, has led to a good yield of the isocoumaranone XXVI (R = CH_3). This substance is a solid which melts at 126.5–128°; when steam distilled, it is transformed into the two products obtained by Smith and MacMullen, *viz.*, the isocoumaranone I and the coumaron II. Neither the intermediate III nor the coumaron acid (XXVIII, R = CH_3) was obtained, although these substances may have been formed in small amounts and lost in the purification of the main product, which required several crystallizations.

Experimental Part[10]

Acetylacetone and acetylisobutyrylmethane were prepared by the method of Sprague, Beckham and Adkins.[11] **Acetylacetone** was distilled several times through a Widmer column and the fraction boiling at 135–136°, obtained in 27% yield, was used. **Acetylisobutyrylmethane**, purified in a similar manner, boiled at 159–161° and was obtained in 20% yield.

Trimethylquinone (VII) was prepared by the method of Smith, Opie, Prichard and Wawzonek.[12]

(3,6 - Dihydroxy - 2,4,5 - trimethylphenyl) - acetylacetone, VIII.—Acetylacetone (3.8 g., 0.038 mole) was added to alcoholic sodium ethoxide (prepared from sodium, 0.75 g., 0.0326 mole, and dry ethanol, 12 cc.). The solution was cooled (0°) and stirred, and to it was added slowly (twelve hours) a solution of trimethylquinone (2.25 g., 0.015 mole) in dry ethanol (30 cc.). The resulting deep purple solution was stirred for an hour at room temperature, and then, with cooling (0°) and stirring, concd. hydrochloric acid was added dropwise until the color changed to light yellow. The acidified mixture was poured over cracked ice (300 g.) and the solid (2.7 g.) was removed and crystallized from benzene–petroleum ether (b. p. 90–100°). The product was white and melted at 129–130°.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.16; H, 7.21. Found: C, 67.47; H, 7.28.

Reaction with Phenylhydrazine.—The diketone VIII (0.32 g.) was dissolved in ethanol and water was added until the first trace of turbidity resulted. Phenylhydrazine (0.5 cc.) and acetic acid (1 drop) were added. A solid precipitated almost immediately. After standing overnight, this was removed and crystallized from ethanol. It weighed 0.43 g., and melted at 205–206° with decomposition. The structure was not investigated.

Anal. Found: C, 69.41; H, 6.94.

2,4,6,7-Tetramethyl-5-hydroxycoumaron (II).—The diketone VIII (0.5 g.) was refluxed with concd. hydrochloric acid (30 cc.) and ethanol (1 cc.) for three and one-half hours. Water (70 cc.) was added and the mixture was steam distilled. The product (0.3 g.) was isolated from the distillate and crystallized from dilute ethanol. It melted at 138–139°, alone or when mixed with an authentic specimen.[3]

2,4,6,7-Tetramethyl-5-acetoxycoumaron IX.—The coumaron II (0.5 g.) was acetylated in the usual way with acetic anhydride (2.1 cc.) and a drop of sulfuric acid. The product (0.46 g.) after crystallization from dilute ethanol, melted at 91–92°.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.92. Found: C, 72.13; H, 7.12.

(3,6-Diacetoxy-2,4,5-trimethylphenyl)-acetone X.—The diketone VIII (1.04 g.) was acetylated with acetic anhydride (6.2 cc.) and a drop of sulfuric acid. The reaction was slightly exothermic and the diketone slowly dissolved. After standing at room temperature for an hour, the mixture was poured over ice (75 g.). The product (0.99 g., 81%) melted at 130–132°; after crystallization three times from petroleum ether (b. p. 90–100°), it melted at 135.5–136.0°. The material gave a negative Folin test and was insoluble in cold 10% sodium hydroxide. Attempts to remove the acetyl groups from this ketone invariably gave either unchanged material or the coumaron II. Dilute (0.12 *N*) hydrochloric acid was without action during eight hours at 65°; the action of more concentrated acid (1 *N*) at 100° for seven hours led to a mixture of starting material and II; while concentrated acid (12 *N*) gave only the coumaron. Likewise dilute sodium hydroxide gave only the coumaron.

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.71; H, 6.91. Found: C, 65.91; H, 7.42.

Oxime XI.—The oxime (0.12 g.) was prepared from the ketone X (0.16 g.) in the usual way. The crude product melted at 160–162°; after several crystallizations from dilute ethanol, the monoxime melted at 172–175° with decomposition. The oxime dissolves immediately in 10% sodium hydroxide, giving a yellow solution,

---

[8] Bergel, Jacob, Todd and Work, *J. Chem. Soc.*, 1375 (1938).

[9] Karrer, Escher and Rentschler, *Helv. Chim. Acta.* **22**, 1287 (1939).

[10] Microanalyses by J. W. Opie, H. H. Hoehn and C. O. Guss.

[11] Sprague, Beckham and Adkins, THIS JOURNAL, **56**, 2665 (1934).

[12] Smith, Opie, Prichard and Wawzonek, *J. Org. Chem.*, **4**, 318 (1939).

Anal. Calcd. for $C_{16}H_{21}O_5N$: C, 62.48; H, 6.90; N, 4.56. Found: C, 63.02; H, 7.18; N, 4.55.

(3-Isobutyroxy-6-acetoxy-2,4,5-trimethylphenyl)-acetone, XVII.—The diketone VIII (0.53 g., 0.0021 mole) was dropped into isobutyric anhydride (5.3 cc.) and sulfuric acid (2 drops) at room temperature. After two hours, all of the solid dissolved. After seven hours, the mixture was poured over ice (75 g.) and concd. ammonium hydroxide (8 cc.) was added. The solid was removed and washed thoroughly with water. It weighed 0.38 g. (56%) and melted at 117.5–123°. After crystallization from petroleum ether, the white solid melted at 127.5–128°. It gave a negative Folin phenol test.

Anal. Calcd. for $C_{18}H_{24}O_5$ (XVII): C, 67.46; H, 7.57; mol. wt., 320. Calcd. for $C_{22}H_{30}O_6$ (diisobutyrate of VIII): C, 67.66; H, 7.75; mol. wt., 390. Found: C, 67.55; H, 7.43; mol. wt. (Rast), 336, 302.

(3-Chloroacetoxy-6-acetoxy-2,4,5-trimethylphenyl)-acetone, XVIII.—The diketone VIII (0.53 g., 0.0021 mole) was warmed (45–50°) with chloroacetic anhydride (6 g., 0.0033 mole) for an hour and fifteen minutes. The mixture was poured onto ice (75 g.) and allowed to stand for fifteen minutes. The oily solid was removed and washed several times with small portions of petroleum ether (b. p. 28–38°). It melted at 47–53° and was contaminated with much chloroacetic anhydride. The aqueous filtrate, on standing overnight, deposited 0.1 g. (17.5%) of a white solid (XVIII), which after several crystallizations from benzene–petroleum ether (b. p. 90–100°) melted at 162–163°. Although the yield of pure solid was poor, the actual yield of product was undoubtedly much higher. This substance gave a strongly positive Folin test, which, however, was of little consequence since chloroacetic anhydride itself gave a positive test.

Anal. Calcd. for $C_{16}H_{19}O_5Cl$: C, 58.79; H, 5.85. Found: C, 59.02; H, 6.29.

(3,6-Dihydroxy-2,4,5-trimethylphenyl)-acetylisobutyrylmethane XII.—Acetylisobutyrylmethane (10 g., 0.078 mole) was added to alcoholic sodium ethoxide (prepared from sodium, 1.51 g., 0.066 mole, and dry ethanol, 14 cc.). The solution was cooled (0°) and stirred, and to it was added slowly (two hours) a solution of trimethylquinone (4.95 g., 0.033 mole) in dry ethanol (20 cc.). Stirring was continued for half an hour at room temperature after the addition, and then, with cooling (0°) and stirring, concd. hydrochloric acid was added dropwise until the deep violet color changed to yellow. The acidified mixture was poured onto ice (250 g.), the solid was removed and washed three times with petroleum ether (25 cc. each time, b. p. 40–70°) and once with water (25 cc.). The product XII weighed 7.43 g. (81%). After crystallization from dilute ethanol or benzene–petroleum ether (b. p. 90–100°) the substance formed colorless needles which melted at 131.5–132.5°.

Anal. Calcd. for $C_{16}H_{22}O_4$ (XII): C, 69.02; H, 7.97. Calcd. for $C_{12}H_{16}O_3$ (X, $R^1 = R^2 = H$): C, 69.30; H, 7.67. Found: C, 69.36; H, 7.98.

Reaction with Phenylhydrazine.—The diketone XII (0.32 g.) reacted with phenylhydrazine (0.5 cc.) and acetic acid (3 drops) in dilute alcohol, to give a product (0.3 g.) which melted at 167° with decomposition. The structure of this compound was not investigated.

(3-Acetoxy-6-isobutyroxy-2,4,5-trimethylphenyl)-acetone XIV.—The diketone XII (1.64 g., 0.0059 mole) was dropped into acetic anhydride (12 cc.) containing a drop of sulfuric acid. The mixture became warm, and the solid dissolved. After standing for an hour, the solution was poured onto ice (75 g.). The solid was removed, washed with water, and dried. It weighed 1.44 g. After crystallization from petroleum ether (b. p. 90–100°), the solid weighed 0.52 g. and melted at 114–115.5°.

Anal. Calcd. for $C_{18}H_{24}O_5$: C, 67.46; H, 7.57. Found: C, 67.19; H, 7.27.

The filtrate on evaporation, left a mixture which melted at 100–115°.

When the ketone XIV (0.25 g.) was refluxed with concd. hydrochloric acid (17 cc.) for two and one-half hours, the product (0.13 g.) was the coumaron II, m. p. and mixed m. p., 137–138°.

Anal. Calcd. for $C_{12}H_{14}O_2$ (II): C, 75.75; H, 7.42. Calcd. for $C_{14}H_{18}O_2$ (XIII): C, 76.99; H, 8.33. Found: C, 75.57, 75.42; H, 7.81, 7.60.

Oxime XV.—The ketone XIV (0.24 g.) was converted to the oxime (0.1 g.) in the usual way. After crystallization from dilute ethanol, the product melted at 165–170° with decomposition. When mixed with the oxime XI, the substance melted at 150–160°.

Anal. Calcd. for $C_{18}H_{25}O_5N$: C, 64.41; H, 7.56; N, 4.18. Found: C, 64.50; H, 7.47; N, 4.51.

Cyclization of XII.—The diketone (0.53 g., 0.0019 mole) was refluxed for two and a half hours with concd. hydrochloric acid (25 cc.) and ethanol (1 cc.). The reaction mixture, after dilution with water, was steam distilled. The white solid (0.36 g.) which was removed from the distillate melted at 100–125°. This mixture probably consisted of the coumarons II and XIII, but the amount of material available was too small for fractional crystallization.

Addition of Other Diketones.—(a) Trimethylquinone (0.65 g.) was added to the sodium enolate of *n*-butyrylacetylmethane (from 1.3 cc. of diketone) in dry ethanol as described for the addition of acetylacetone. The only product was an oil which could not be crystallized. (b) The quinone (1.65 g.) in dry ethanol (10 cc.) was added to a suspension of sodium benzoylacetone (sodium, 0.58 g., diketone, 4.1 g., ethanol, 10 cc.) in the same manner. Only a few milligrams of a tan solid, m. p. 110–120°, was obtained. (c) The quinone (0.75 g.) in ethanol (10 cc.) was added to a suspension of the enolate of dibenzoylmethane (sodium, 0.21 g., diketone, 2.20 g., ethanol, 30 cc.) as described. The only product was dibenzoylmethane, m. p. and mixed m. p. 74–76°.

3-Acetyl-4,6,7-trimethyl-5-hydroxyisocoumaranone (XXVI, R = CH_3).—Acetoacetic ester (5.7 g.) was added to a solution of sodium ethoxide prepared from sodium (0.97 g.) and dry ethanol (20 cc.). The quinone (3.1 g.) in ethanol (2 cc.) was gradually added and the deep purple solution was allowed to stand at room temperature for three and one-half hours. The reaction mixture was poured into ice (200 g.) and hydrochloric acid (20 cc.). The product appeared as an oil which soon crystallized to a tan solid (4.5 g.) melting at 100–121°. Repeated crystallization from benzene–petroleum ether (b. p. 90–100°) gave white needles (2.58 g.) which melted at 126.5–128°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.64; H, 6.03. Found: C, 66.48, 67.00; H, 5.88, 6.19.

The substance is relatively stable toward heat and inert solvents, but is unstable toward polar solvents. It is insoluble in sodium carbonate and in sodium bicarbonate solutions. No ether was formed using either methyl sulfate or diazomethane, nor could an oxime be obtained.

When the acetylisocoumaranone (0.4 g.) was steam distilled, coumaron II (0.07 g.), m. p. and mixed m. p. 137–138°, was isolated from the distillate and the isocoumaranone I (0.26 g.), m. p. 200.5–202.5°,[13] remained in the flask.

Summary

1. The sodium enolates of acetylacetone and isobutyrylacetylmethane react with trimethylquinone to give (3,6-dihydroxy-2,4,5-trimethylphenyl)-acetylacetone (VIII) and -acetylisobutyrylmethane (XII), respectively. No pure substances could be isolated from the product of the reaction between the quinone and the enolates of *n*-butyrylacetylmethane or benzoylacetone, and only unchanged diketone was isolated when the enolate of dibenzoylmethane was used.

2. Acylation of the diketones VIII and XII involves a rearrangement of one of the side chain acyl groups from carbon to the *ortho*-oxygen atom; simultaneously, the other hydroxyl group is acylated by the reagent used. A mechanism is suggested for this rearrangement.

3. An intermediate has been isolated from the reaction between trimethylquinone and sodium acetoacetic ester. This intermediate, when steam distilled, gives the final products obtained previously in a study of this reaction.

MINNEAPOLIS, MINNESOTA

RECEIVED NOVEMBER 10, 1939

---

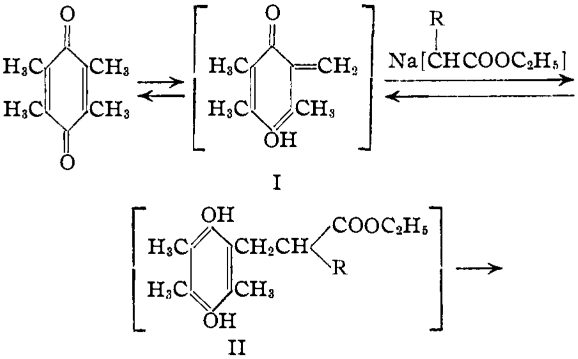
[13] The m. p. previously reported was 197–198°.

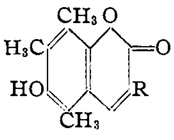
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Quinones and Metallic Enolates. XI. Duroquinone and the Enolates of Cyanoacetic Ester and of β-Diketones[1]

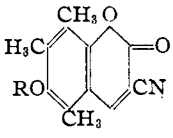
BY LEE IRVIN SMITH AND E. W. KAISER[2]

The reaction between duroquinone and sodium malonic ester,[3] was extended to other tetrasubstituted quinones by Webster,[4] who used 2,3-dimethyl-1,4-naphthoquinone, and by Johnson,[5] who used trimethylbromoquinone. Tenenbaum[6] varied the enolate by using sodium acetoacetic ester, but in all these cases the reaction led to a substituted coumarin (III, IV), and evidence was supplied by Horner[7] that the quinone was first converted into a "pentad-enolate" (I) which then underwent a Michael reaction with the other enolate. The first product (II) was cyclized and oxidized, leading to the coumarin as the final product. In every case so far studied, the enolate used contained an ester group so that the ring closure, by elimination of an alcohol, took place easily, and it has been thought that this easy ring closure was in large part responsible for driving the series of reactions to completion, since the first step presumably, and the second step certainly, are reversible. In order to explore still further the limits of this reaction, the enolates of cyanoacetic ester and of two β-diketones (acetylacetone





III, R = $COOC_2H_5$
IV, R = $COCH_3$
V, R = H
VI, R = Ac



VII, R = $CONH_2$
VIII, R = COOH
IX, Diacetate of VII

---

[1] Paper X, THIS JOURNAL, **62**, 133 (1940).

[2] Abstracted from a Thesis by E. W. Kaiser, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, August, 1939.

[3] Smith and Dobrovolny, THIS JOURNAL, **48**, 1693 (1926).

[4] Smith and Webster, *ibid.*, **59**, 662 (1937).

[5] Smith and Johnson, *ibid.*, **59**, 673 (1937).

[6] Smith and Tenenbaum, *ibid.*, **59**, 667 (1937).

[7] Smith and Horner, *ibid.*, **60**, 676 (1938).