[Contribution from the School of Chemistry of the University of Minnesota]

THE REACTION BETWEEN QUINONES AND METALLIC ENOLATES. XXV. TRIMETHYLQUINONE AND THE ENOLATES OF CYANOACETIC ESTER, CYANOACETAMIDE, BENZYL CYANIDE, OXALOACETIC ESTER, AND THE ACETAL OF DIACETYL (1)

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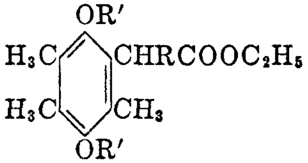
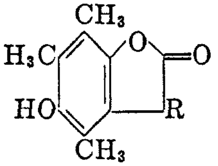
Previous work dealing with the reaction between trimethylquinone and various metallic enolates (2–7) has shown that the reaction involves a primary 1,4-addition to the open conjugated system in the quinone, to give a hydroquinone (I). Often the hydroquinone can be isolated only with difficulty; in these cases, the chief product of the reaction is one derived from the hydroquinone by ring closure. Thus, with the enolates of malonic ester, the products are the hydroquinone I and the isocoumaranone II derived from I by loss of the elements of ethanol; this reaction may or may not be accompanied by the loss of a carboethoxyl group.

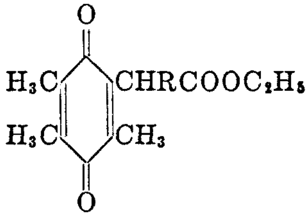


I $R = COOC_2H_5; R' = H$

III $R = CN; R' = H$



II $R = COOC_2H_5$ or H



IV $R = CN$

To explore further this reaction, and particularly to explore the structural features of the enolate which limit the reaction, a study has been made of the reaction between trimethylquinone and the enolates of cyanoacetic ester, cyanoacetamide, benzyl cyanide, oxaloacetic ester, and the mono acetal of diacetyl.

A. *Sodio ethyl cyanoacetate.* No pure product could be obtained when this enolate was condensed with trimethylquinone in ethanol, but in dry, peroxide-free dioxane, the hydroquinone III was obtained in small (up to 32%) yields. Although purple and red colors were developed during the reaction, the hydroquinone III was itself not colored. This is in contrast with the purplish-red *bis*-cyanoacetic ester addition product obtained by Wood, Colburn, Cox, and Garland (8) from cyanoacetic ester and the unsubstituted *p*-benzoquinone when ammonia was used as the condensing agent; this highly colored substance was shown by these authors to be quite analogous to III in structure.

The hydroquinone III was converted, by action of ferric chloride, into the orange-yellow quinone IV. The hydroquinone was readily acetylated, but the

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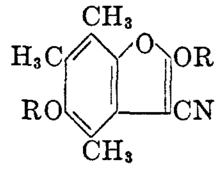
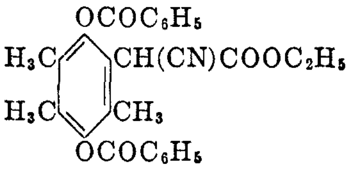
[1] Abstracted from a thesis by Wesley J. Dale, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, August, 1949. National Research Council Fellow, 1946–1949.

products were mixtures very difficult to separate into pure compounds. Action of acetic anhydride and pyridine upon III gave ill-defined results, but action of acetic anhydride and sulfuric acid produced the enol acetate of the acetoxyisocoumaranone V.



V R = Ac

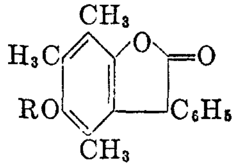
VII R = C_6H_5CO



VI

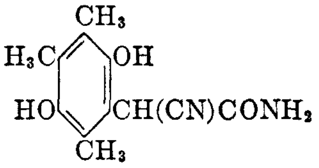
Action of benzoyl chloride and pyridine upon III produced a mixture of the corresponding hydroquinone dibenzoate VI and the enol benzoate VII. When the hydroquinone III was subjected to the action of ethanol and sulfuric acid, the product was the known isocoumaranone II, R = H (2), formed by cyclization and elimination of the cyano group.

B. *Benzyl cyanide.* When the enolate of benzyl cyanide was condensed with trimethylquinone in methanol, the only product isolated (32%) was the hydroxyisocoumaranone VIII. This substance contained no nitrogen; the reaction therefore involved addition of the cyanide with subsequent hydrolysis of the nitrile group and elimination of water to give the cyclized product. The isocoumaranone VIII, when acetylated, gave only the monoacetate IX; no enol acetate was formed.



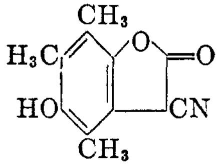
VIII R = H

IX R = Ac

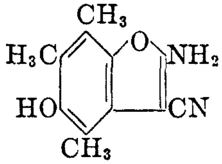


X

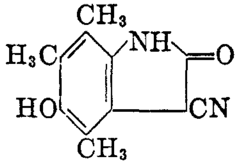
C. *Cyanoacetamide.* The enolate of cyanoacetamide would be expected to react with trimethylquinone to produce the hydroquinone X and/or a derivative of it formed by subsequent ring closure.



XI



XII



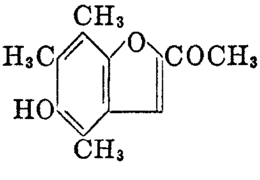
XIII

Excluding any products derived from X by hydrolysis of the cyano or amide groups, the further transformations of X would be expected to lead to the cyanoisocoumaranone XI (loss of ammonia) or, by loss of water, to the amino coumaron XII or to the hydroxyindolone XIII. The product of the reaction between trimethylquinone and cyanoacetamide was a white substance melting at 240–245° which gave a positive Folin test. Action of acetic anhydride upon this product produced a diacetate, and action of benzoyl chloride produced a dibenzoate. The found analytical values, compared with those required by structures X, XI, and XII (XIII) and their respective diacetates and dibenzoates, are as follows:

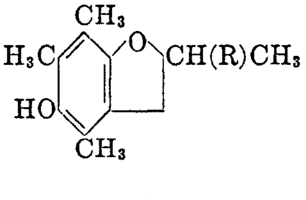
PARENT COMPOUNDS	C	H	N
X ($C_{12}H_{14}N_2O_3$)	61.52	6.02	11.96
XI ($C_{12}H_{11}NO_3$)	66.35	5.11	6.45
XII, XIII ($C_{12}H_{12}N_2O_2$)	66.65	5.60	12.96
Found:	66.69	5.77	12.73, 12.91
DIACETATES			
of X ($C_{16}H_{18}N_2O_5$)	60.37	5.70	8.80
of XI ($C_{16}H_{15}NO_5$)	63.80	5.02	4.65
of XII, XIII ($C_{16}H_{16}N_2O_4$)	63.99	5.38	9.33
Found:	63.67, 64.08	5.42, 5.46	9.24, 9.14
DIBENZOATES			
of X ($C_{26}H_{22}N_2O_5$)	70.58	5.02	6.33
of XI ($C_{26}H_{19}NO_5$)	72.50	4.65	3.39
of XII, XIII ($C_{26}H_{20}N_2O_4$)	73.57	4.75	6.60
Found:	73.53, 73.36	4.82, 5.03	6.63, 6.69

These data served to fix the course of the reactions quite definitely: the product is derived from one molecule each of the quinone and cyanoacetamide, followed by loss of water from the primary product X. Calculated upon this basis, the yield of recrystallized product was 74–83%. Structure XII was assigned to this product although the isomeric structure XIII cannot be entirely excluded.

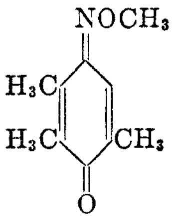
D. If the condensation between trimethylquinone and diacetyl or a suitable derivative of the diketone could be achieved, a route would be opened to coumarons of the type of XIV, and from these, by obvious methods, to coumarans of type XV.



XIV



XV



XVII

$CH_3COC(OCH_3)_2CH_3$

XVI

However, diacetyl itself does not undergo a base-catalyzed condensation with trimethylquinone, for the basic catalyst brings about self condensation of the diketone too rapidly. The mono acetal XVI of diacetyl is, however, stable toward sodium ethoxide and other bases. It appeared worth while to study the behavior of the enolate of XVI toward trimethylquinone, although Smith and Prichard (3) had found that the enolates of α,α-disubstituted acetoacetic esters could not be condensed with the quinone, even when the γ-hydrogen atoms were activated by the presence of a cyano or carbethoxyl group attached to the γ-carbon atom. Sodium ethoxide was without action upon XVI, and when sodium ethoxide was added to a solution of the quinone and XVI in ethanol, the only reaction was degradation of the quinone by action of the alkali. It was obvious, therefore, that a more powerful enolizing agent than sodium ethoxide would be necessary in order to convert XVI into its enolate. It was found that XVI was readily enolized by action of sodium amide (evolution of ammonia), but when trimethylquinone was added to the solution of the enolate, an intense green color developed and no condensation product could be obtained. This appearance of a green color in base-catalyzed reactions of trimethylquinone indicates degradation of the quinone by the base and is produced when the quinone alone is subjected to the action of bases. In all cases in which the quinone has been successfully condensed with an enolate, the colors of the reaction mixture have been brown, red, or purple—never green.

Isopropylmagnesium bromide reacted vigorously with XVI and a gas was evolved. However, when trimethylquinone was added to the solution of the enolate in ether or dioxane, a green color developed, and the only products were unchanged starting materials.

The acetal XVI was also converted into the enolate by action of powdered sodium at −15°. That XVI was in the form of the enolate was shown by hydrolysis of the enolate, by action of acid, to diacetyl and identification of the diketone as the dioxime, isolated in 66% yield. However, the sodium enolate of XVI, prepared in this manner, failed to condense with trimethylquinone. The reaction mixture developed the characteristic green color, and no pure product could be isolated from it.

In contrast with the quinone, the 1-monoxime methyl ether XVII (10) of the quinone is stable toward alkali. When the sodium enolate of XVI was added to a solution of XVII in ether, the reaction mixture did not develop the green color characteristic of unsuccessful condensations of the quinone, but became brownish-red and deposited a bluish-red solid. From this reaction mixture, acidic, neutral, and basic fractions were obtained, but no pure product could be isolated from any of these fractions.

E. When the attempts to condense trimethylquinone with the acetal XVI resulted in failure, attention was turned to ethyl oxalacetate, for successful condensation of trimethylquinone with the enolate of this substance would lead to a coumaron substituted in the hetero ring by carbethoxyl groups. These groups could then be manipulated so that coumarons and coumarans with various side chains could be synthesized. However, under none of the conditions tried, could any products other than dark, intractable tars, be obtained from trimethylquinone and the enolate of oxalacetic ester. The conditions included use of the sodium enolate in dioxane or pyridine, and reaction of the quinone with the ester in the presence of a catalytic amount of piperidine. Under the latter conditions, there was no reaction at all and the starting materials were recovered completely.

EXPERIMENTAL PART[2]

A. *Ethyl 2,5-dihydroxy-3,4,6-trimethylphenyl-α-cyanoacetate.* (III). Trimethylquinone (15 g., 0.1 mole) in dry, peroxide-free dioxane (9) (20 cc.) was slowly (70 minutes) added dropwise and with stirring and cooling (15°) to a suspension of sodio ethyl cyanoacetate (from sodium, 2.3 g., and ethyl cyanoacetate 11.7 cc.) in dioxane (70 cc.). The purple suspension was stirred at 15° for an hour, then cooled to 5° while hydrochloric acid (9.5 cc.) was adcdd dropwise. The orange-brown slurry was poured, slowly and with stirring, into ice and water (1 l.). The brown putty-like mass was removed, dissolved in ether, the solution was washed with water until the washings were neutral, and dried (sodium sulfate). The solvent was removed; the residue (26 g.), a syrup containing some solid, was triturated twice with hot petroleum ether (150 cc., b.p., 60–68°) to remove unchanged quinone. The residue wsa dissolved in ether and the solution was washed several times with aqueous sodium hydrosulfite, dried, and the solvent was removed. The dry residue (20 g.), crystalline and brick-red, was extracted six times with boiling (60–68°) petroleum ether (300 cc. each time) and the filtered (hot) extracts were combined and cooled (−15°) in a refrigerator overnight. The gray-white solid was removed and crystallized from aqueous ethanol (50%), when it melted at 155.5–156°. The Folin test was positive.

Anal. Calc'd for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32.
Found: C, 63.54; H, 6.75; N, 5.36.

The hydroquinone III was recovered unchanged when a solution of it in sulfuric acid was warmed to 40°. When III (0.7 g.) was subjected to the action of 81% sulfuric acid at 100° for 3 hours, the only product was a black powder (0.2 g.).

The hydroquinone (1 g.) in ethanol (25 cc.) was refluxed with sulfuric acid (4 cc.) for 5 hours; the solution was poured into water, the solid (0.7 g.) was removed and crystallized successively from aqueous ethanol and benzene-petroleum ether. It then melted at 194.5–196°, and was the coumaron II, R = H (2).

2,5-Diacetoxy-3-cyano-4,6,7-trimethylcoumaron (V). A solution of the hydroquinone III (1 g.) in acetic anhydride (15 cc.) containing sulfuric acid (1 drop) was warmed for 2 hours, then poured into ice-water and allowed to stand for 4 hours. The solid was removed, dissolved in hot ethanol (45 cc.), and the solution was slowly cooled to room temperature. The white clusters weighed 0.09 g. (8%) and melted at 225–230°. After recrystallization twice from ethanol, the substance showed the same melting point.

Anal. Calc'd for $C_{16}H_{15}NO_5$: C, 63.87; H, 5.02; N, 4.65.
Found: C, 64.01; H, 5.25; N, 4.68.

The mother liquors, when diluted with water, deposited 1.2 g. of solid melting at 95–120°. This mixture could not be separated into pure materials by crystallization from ethanol; when chromatographed from benzene onto alumina, a small amount of material melting at 137–137.5° was obtained. The analytical values of this material did not correspond with those required by any reasonable structure derived from V. When V (0.4 g.) was acetylated by action of acetic anhydride (7 cc.) in pyridine (10 cc.), there was obtained a material melting at 135–138°, not identical with that of m.p. 137–137.5° above. After

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[2] Microanalyses by Roger Amidon, Jay S. Buckley, and William Cummings.

crystallization several times from aqueous ethanol and benzene-petroleum ether, this material melted at 142–144.5°, but no reasonable structure could be written for it.

Anal. Found: C, 65.06; H, 6.62; N, 4.41.

Ethyl α-cyano-2,5-dibenzoyloxy-3,4,6-trimethylphenylacetate (VI). Benzoyl chloride (2 cc.) was added to a solution of the hydroquinone III (0.26 g.) in pyridine (8 cc.). The solution was boiled for 5 minutes, cooled, and poured into water (20 cc.). Ethanol was added until a yellow solid deposited; this solid was removed (see below) and the filtrate was diluted with water and set aside in a refrigerator. The white solid (0.32 g., m.p., 155–160°) was removed and crystallized from ethanol, when it still melted at 155–160°. It was then dissolved in benzene and the solution was passed through a column of alumina. The column was eluted with benzene (750 cc.), leaving a yellow band on the column. The eluate, on evaporation, left 0.14 g. of product melting at 171–175°. The analytical sample, crystallized from ethanol, melted at 178–179.5°.

Anal. Calc'd for $C_{26}H_{25}NO_6$: C, 71.32; H, 5.35; N, 2.97.
Found: C, 71.50; H, 5.61; N, 3.09.

2,5-Dibenzoyloxy-3-cyano-4,6,7-trimethylcoumaron (VII). The yellow solid (0.1 g.) obtained from the above preparation of VI was recrystallized several times from chloroform-ethanol, when it melted at 266–267.5°.

Anal. Calc'd for $C_{26}H_{19}NO_5$: C, 73.40; H, 4.50; N, 3.29.
Found: C, 73.65; H, 4.54; N, 3.23.

Ethyl 3,5,6-trimethylquinone-2-α-cyanoacetate (IV). A solution of the hydroquinone III (0.7 g.) in ethanol (15 cc.) was added to a solution of ferric chloride (5 g.) in water (5 cc.) and hydrochloric acid (4 drops). The solution, after standing for 90 minutes, deposited an orange-yellow solid. The solution was diluted with water (10 cc.) and set aside in a refrigerator. The product (0.34 g.) was removed, washed with water, and dried, when it melted at 230° (dec.). This material was dissolved in ether and the solution was passed through a column (1.4 × 13 cm.) of alumina (80–200 mesh). The filtrate was concentrated to 7 cc. and diluted with petroleum ether (b.p., 28–38°). The solid (m.p., 247–250°) was removed and crystallized three times from aqueous acetone, when it melted at 251.5–253° (dec.).

Anal. Calc'd for $C_{14}H_{15}NO_4$: C, 64.35; H, 5.79.
Found: C, 64.21; H, 5.65.

B. *3-Phenyl-4,6,7-trimethyl-5-hydroxyisocoumaranone* (VIII). Benzyl cyanide (12.7 cc., 0.11 mole) was added dropwise and with stirring to a solution of sodium methoxide in methanol (from sodium, 2.3 g., and methanol, 30 cc.). Stirring was continued for 10 minutes, and then, with continued stirring, a solution of trimethylquinone (15 g., 0.1 mole) in methanol (10 cc.) was added dropwise. The mixture was allowed to stand at room temperature for 2 days, and was then poured onto ice (200 g.) containing hydrochloric acid (10 cc.). The solid was removed, dissolved in ether, and the solution was filtered to remove a small amount (0.2 g.) of red material. The filtrate was washed with water until the washings were neutral, dried, and the solvent was removed. The dark residue (25.2 g.) was a brown, semi-solid mass. A portion (12.4 g.) was dissolved in hot benzene (60 cc.), the solution was boiled for one minute with Norit, filtered, and the filtrate was concentrated to 45 cc. and set aside for several days. The solid (4.2 g., 32%) was crystallized several times in an atmosphere of nitrogen from benzene-petroleum ether, when it melted at 152.5–157.5°. Solutions of VIII were sensitive to air.

Anal. Calc'd for $C_{17}H_{16}O_3$: C, 76.00; H, 6.00.
Found: C, 76.12; H, 6.08.

3-Phenyl-4,6,7-trimethyl-5-acetoxyisocoumaranone (IX). A solution of VIII (0.65 g.) in acetic anhydride (17 cc.) and sulfuric acid (1 drop) was heated to the boiling point, then cooled and poured into water. The solid (0.8 g.) was removed, washed with water, and dried. It then melted at 205–206°; after several crystallizations from ethanol, it melted at 207–208°.

Anal. Calc'd for $C_{19}H_{18}O_4$: C, 73.52; H, 5.85.
Found: C, 73.60; H, 5.85.

C. *2-Amino-3-cyano-4,6,7-trimethyl-5-hydroxycoumaron* (XII) [or *3-Cyano-4,6,7-trimethyl-5-hydroxyindolone* (XIII)]. A solution of sodium methoxide (from sodium, 2.3 g., and methanol 60 cc.) was added, dropwise and with stirring, to a solution of cyanoacetamide (10.1 g., 0.12 mole) in methanol (30 cc.). To the clear solution of the enolate, a solution of trimethylquinone (15 g., 0.1 mole) in methanol (10 cc.) was added, dropwise and with stirring. During these operations, the reaction mixture was carefully protected from moisture. Heat evolved during the reaction was sufficient to cause the solution to reflux gently; after addition was complete, the mixture was stirred and refluxed for 20 minutes and was then allowed to stand overnight. The cooled (5°) mixture was stirred while hydrochloric acid (9.5 cc.) was added dropwise; the whole was then vigorously stirred into ice and water (1 l.), and allowed to stand for 3 hours. The solid (20.5 g.) was washed with water, dried, and dissolved in dioxane (200 cc.). The solution was filtered and the filtrate was cooled (10°). The crystalline product (16.9 g., 78%) was slightly pink, but could be obtained completely free of color by several crystallizations from dioxane. The pure substance melted at 240–245° (dec.) with previous darkening at 220–230°. The analytical values are given in the table.

Diacetate. A solution of XII (1.3 g) in acetic anhydride (10 cc.) and sulfuric acid (1 drop) was boiled for one minute and then poured into water. The solid was removed and crystallized several times from small volumes of ethanol, when it melted at 226–227.5°. The analytical values are given in the table.

Dibenzoate. A solution of XII (1 g.) and benzoyl chloride (2 cc.) in dry pyridine (6 cc.) was boiled for one minute, then cooled and poured into water. The solid was crystallized several times from large volumes of ethanol, when it melted at 238.5–241°. The analytical values are given in the table.

D. A solution of trimethylquinone (3 g.) and XVI (2.64 g.) in dry ethanol was added to a solution of sodium ethoxide (from sodium, 0.46 g., and ethanol, 5 cc.). The black reaction mixture was allowed to stand for 24 hours, then was poured onto ice and hydrochloric acid (5 cc.) and steam-distilled. The distillate contained a small amount of diacetyl; the residue was a black resin. Essentially the same results were obtained when the experiment was repeated and dioxane was substituted for ethanol.

A solution of XVI (6.9 g.) in benzene (25 cc.) was added to a solution of sodium amide (from sodium, 1.15 g., and liquid ammonia, 100 cc.) in benzene (75 cc.). The temperature rose, and ammonia was evolved. The solution was stirred for 20 minutes and then a solution of trimethylquinone (7.5 g.) in benzene (25 cc.) was added dropwise. A green color developed at once. The mixture was stirred and refluxed for 2 hours, then cooled and stirred with hydrochloric acid (10%, 100 cc.). The benzene layer was removed, washed with water, and dried. Removal of the solvent left an amorphous, brown, tarry resin, which resisted all attempts at crystallization. The same results were obtained where the experiment was repeated and dioxane was substituted for benzene.

A solution of XVI (2.9 g.) in ether (20 cc.) was added to a solution of isopropylmagnesium bromide (from magnesium, 0.54 g., isopropyl bromide, 2.5 g.) in ether (20 cc.). Evolution of gas occurred, and a voluminous white precipitate separated. The mixture was stirred while a solution of trimethylquinone (3 g.) in ether (20 cc.) was added; thereafter, the mixture was refluxed for 4 hours. A green color developed within 10 minutes after the quinone was added. The mixture was poured onto hydrochloric acid (5%, 75 cc.) and steam-distilled. The distillate contained trimethylquinone and diacetyl; the residual liquid in the distillation flask contained only traces of organic material. When the experiment was repeated and dioxane was substituted for ether, the results were the same except that a black resinous material remained in the distillation flask.

To a cooled (−15°) suspension of powdered sodium (0.9 g.) in ether (30 cc.), the acetal XVI (6.35 g.) was added in small portions. After 2 hours, the metal had dissolved; the cold solution was acidified with hydrochloric acid (5 cc. in water, 10 cc.). The solution was stirred vigorously at room temperature; the ether layer was removed and the aqueous layer was extracted three times with ether. The combined ether solutions were dried; hydroxylamine hydrochloride (13.3 g.) in water (100 cc.) was added, followed by addition of sodium carbonate (10.2 g.) in water (100 cc.). The mixture was shaken for 15–20 minutes, ether was removed by distillation, and the aqueous solution was concentrated and cooled. The solid (3.7 g., 66%) melted at 230–232°, alone or when mixed with an authentic specimen of dimethylglyoxime. To a solution of the enolate of XVI, prepared as described above, trimethylquinone (6 g.) in ether (20 cc.) was added dropwise. A green color developed at once; the mixture was stirred with aqueous hydrochloric acid (1:1); the ether layer was separated, dried, and the solvent was removed by distillation. The residue, when evaporatively distilled at 0.001 mm. and 100°, yielded a small amount of trimethylhydroquinone formed by reduction of the quinone. No other pure material could be isolated.

Results similar to the above were obtained when the monoxime methyl ether XVII was substituted for trimethylquinone in experiments involving the sodium enolate of XVI.

E. A solution of sodium ethoxide (from 1.4 g. of sodium) in ethanol (20 cc.) was diluted with dioxane (20 cc.). To this was added a solution of ethyl oxalacetate (11.5 cc.) in dioxane (25 cc.). To the suspension of the enolate was added, dropwise and with stirring, a solution of trimethylquinone (3 g.) in dioxane (15 cc.). The dark solution was allowed to stand at room temperature for one week, then was cooled (5°) and stirred while hydrochloric acid (5 cc.) was added dropwise. The solution was poured into ice-water (1 l.), neutralized with sodium bicarbonate, and set aside at room temperature overnight. The aqueous layer was removed by decantation and the oil was dissolved in ethyl acetate. This solution was extracted four times with 100-cc. portions of aqueous sodium bicarbonate (5%). Removal of the solvent from the organic layer left a residue (4.6 g.) of brown, viscous oil. The alkaline extracts were acidified and extracted with ethyl acetate. Removal of the solvent left another brown oil (3 g.). Both oils contained small amounts of crystalline material, a small amount of which was isolated from the oil insoluble in carbonate. This material melted at 183–184.5°, but the amount was too small for characterization. No other solid material could be isolated from either of the oils. Substantially the same results were obtained when the experiment was repeated and pyridine was substituted for dioxane. The neutral fraction weighed 4.3 g.; the acidic fraction weighed 3.5 g. Both were red-brown oils which could not be separated into any pure substances.

When trimethylquinone and oxalacetic ester were dissolved in ethanol containing a small amount of piperidine, there was no reaction—no change in color occurred, and only unchanged starting materials were isolated from the solution.

SUMMARY

1. Trimethylquinone has been condensed with the enolates of several nitrogenous compounds. Ethyl cyanoacetate gave, as the primary product, the expected hydroquinone (III) formed by 1,4-addition of the enolate to the quinone. The hydroquinone has been converted into the quinone IV, the coumaron V, and several other derivatives.

2. Benzyl cyanide behaved in an analogous manner, although the primary addition product was not obtained. Instead, the primary product under the conditions used underwent ring closure to give an isocoumaranone VIII.

3. Cyanoacetamide gave a product derived from the primary hydroquinone by loss of water. This product appears to be the aminocyanocoumaron XII, although the isomeric structure XIII for the hydroxyindolone cannot be entirely excluded.

4. Two enolates of the monoacetal of diacetyl have been prepared, but neither of these enolates could be condensed with trimethylhydroquinone. The only products were black tars resulting from decomposition of the quinone itself.

5. The enolate of ethyl oxalacetate could not be condensed with trimethylquinone: again the only products were those resulting from decomposition of the quinone. Piperidine in catalytic amounts caused no reaction between ethyl oxalacetate and trimethylquinone.

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