

was removed by distillation, and the product distilled to yield 168 g. (1.18 moles, 91% yield based on diketene) of the ketodioxene, b.p. 65–67° (2 mm.), m.p. 12–13°, n_D^{20} 1.4636, d_4^{20} 1.0879¹¹; $\lambda_{\text{max}}^{\text{water}}$ 252.5 m μ (log ϵ 3.94); $\lambda_{\text{max}}^{\text{EtOH}}$ 247.5 m μ (log ϵ 3.92); $\lambda_{\text{max}}^{\text{isooctane}}$ 239.0 m μ (log ϵ 3.93).

*Anal.*¹² Calcd. for C₇H₁₀O₃: C, 59.14; H, 7.09. Found: C, 59.20; H, 7.15.

No reaction took place when the acid catalyst was replaced by diethylamine. Careful fractionation of the product from a large scale experiment showed no fraction identifiable as isopropenyl acetoacetate. The forefractions, n_D^{20} 1.4590–1.4610, contained only traces of acetone, easily removed by water washing, and the later fractions, n_D^{20} 1.4650–1.4680, contained small amounts of dehydracetic acid. With larger amounts of catalysts, ketene and isopropenyl acetate are also formed. Thus in an experiment as above, but with three times as much catalyst, there was obtained only a 70% yield of the adduct, 2% of ketene and 10% of isopropenyl acetate.

2,4-Dimethyl-2-ethyl-6-keto-1,3-dioxene.—Methyl ethyl ketone reacts similarly to yield a water-white liquid, b.p. 70–74° (5 mm.), n_D^{20} 1.4633, d_4^{20} 1.065.

Anal. Calcd. for C₈H₁₂O₃: C, 61.52; H, 7.75. Found: C, 61.20; H, 7.50.

2,4-Dimethyl-2-phenyl-6-keto-1,3-dioxene.—A mixture of acetophenone (120 g.), diketene (84 g.) and *m*-xylenesulfonic acid (0.4 g.) was heated at 90° for 7 hours and then stripped *in vacuo*. Cooling yielded 100 g. of crude adduct, m.p. 75–80°, which crystallized from a mixture of benzene and cyclohexane in shiny white platelets melting at 93.5°. $\lambda_{\text{max}}^{\text{EtOH}}$ 247.5 m μ (log ϵ 3.86); $\lambda_{\text{max}}^{\text{isooctane}}$ 240.0 m μ (log ϵ 3.84).

Anal. Calcd. for C₁₂H₁₂O₃: C, 70.57; H, 5.92. Found: C, 70.21; H, 5.80. Kuhn-Roth¹³ C—CH₃ det.: Calcd. for 1 C—CH₃: 7.35. Found: 8.67, 8.92.

2,2-Dibenzyl-4-methyl-6-keto-1,3-dioxene prepared similarly from dibenzyl ketone and diketene with *p*-toluenesul-

(11) Since the publication of our preliminary communication,¹ we have prepared some 5 kg. of the acetone adduct. The constants here reported are those of our purest product.

(12) Analyses by the Micro-Tech Laboratories, Skokie, Illinois.

(13) The experimental value of 1.2 C-methyls is as much as might be expected, as acetophenone gives only 0.1 C-methyl. Also, as acid hydrolysis may precede oxidation, this is not adduced as structural evidence.

onic acid, and crystallized from benzene melts at 104–105°; $\lambda_{\text{max}}^{\text{EtOH}}$ 252.5 m μ (log ϵ 3.77); $\lambda_{\text{max}}^{\text{isooctane}}$ 246.0 m μ (log ϵ 3.77).

Anal. Calcd. for C₁₉H₁₈O₃: C, 77.53; H, 6.16. Found: C, 78.00; H, 6.25.

Dehydracetic Acid.—A mixture of the acetone adduct (10 g., 0.07 mole), toluene (200 cc.) and calcium acetate (0.1 g.) was heated with solvent take-off for 5 hours, when 4.0 g. (0.069 mole) of acetone had collected in the distillate. The residue was extracted with dilute aqueous sodium carbonate from which 3 g. (51%) of dehydracetic acid was obtained on acidification.

Higher Acetoacetates.—A mixture of the acetone adduct (20 g., 0.14 mole), 1-butanol (20 g., 0.27 mole) and a trace of *p*-toluenesulfonic acid was heated at 100° for 3 hours. Distillation of the product *in vacuo* yielded 21 g. (95%) of *n*-butyl acetoacetate, n_D^{20} 1.4280.

Similarly, a mixture of the acetophenone adduct (13 g.) and methanol (10 cc.) yielded 9 g. of a mixture of acetophenone and methyl acetoacetate.

A mixture of 4 g. of cholesterol, 8 g. of the acetone adduct, 10 cc. of toluene and a trace of *p*-toluenesulfonic acid was refluxed for 5 hours. Distillation *in vacuo* yielded 4 g. of unchanged acetone adduct, and crystallization of the residue from aqueous ethanol gave 4 g. of cholesteryl acetoacetate¹⁴ identical with authentic material (mixed m.p. and I.R. spectra).

Acetoacetanilide.—A solution of 28.4 g. (0.2 mole) of the acetone adduct, 18.6 g. (0.2 mole) of aniline and 1 g. of diethanolamine in 100 cc. of xylene was heated until no more acetone could be detected in the distillate. The mixture was then cooled and acidified with concd. hydrochloric acid until acid to brom phenol blue. The solid which had precipitated and the xylene solution were combined and extracted with dilute aqueous sodium hydroxide from which 16 g. of acetoacetanilide, m.p. 84–85°, was obtained on acidification.

Acknowledgment.—We are deeply indebted to Professor Martin G. Ettlinger for valuable criticism and advice and to the Directors of Messrs. A. Boake, Roberts and Company (Manufacturing), Ltd., for permission to publish.

(14) A. R. Bader, L. O. Cummings and H. A. Vogel, THIS JOURNAL, 73, 4195 (1951).

LONDON, ENGLAND

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

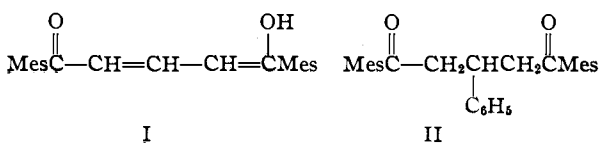
1,5-Diarylpentadienolonates

BY REYNOLD C. FUSON AND L. RUSSELL MELBY

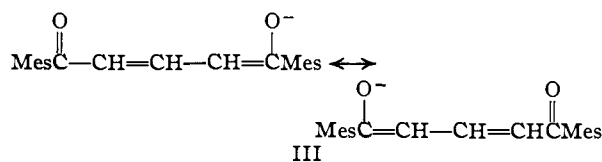
RECEIVED JUNE 1, 1953

Three 1,5-diaryl-1,3-pentadien-1-ol-5-ones have been prepared in which the aryl radicals are mesityl or duryl. The method of synthesis involves the condensation of the bromomagnesium enolates of acetomesitylene and of acetodurene with the enolates corresponding to the hydroxymethylene derivatives of acetomesitylene and acetodurene. The enolates generated from the pentadienolones and the hydroxymethylene compounds are discussed as vinylogs of carboxylate ions.

In spite of the great interest shown in the behavior of glutaconic esters, their analogs in the diketone series have never been described. In the present study it has been possible to prepare examples of this series in which the ketone groups are attached to radicals of the mesityl type. The dimesityl compound, 1,5-dimesityl-1,3-pentadien-1-ol-5-one (I), is a yellow solid and represents a new type of stable enol. It forms an acetate which, as was to be

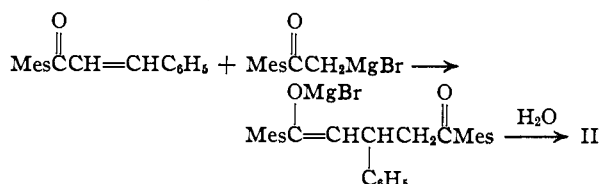


expected, is readily hydrolyzed. It reacts with an excess of phenylmagnesium bromide to give 1,5-dimesityl-3-phenyl-1,5-pentadione (II). The addition reaction involves the completely symmetrical enolate III, which is much more highly stabilized by resonance than the parent enol. The reaction of the enolate with the Grignard reagent illustrates a salient characteristic of such vinylogs of carboxylate ions.



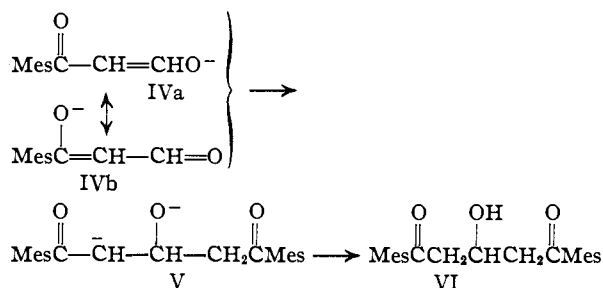
The carbonylic reactivity is abnormally low and the point of greatest electron deficiency is at the central carbon atom. The cationoid character of the enolate is sufficient to permit attack by the phenyl reagent but not by the much weaker reagent, the bromomagnesium enolate of acetomesitylene ($\text{MesCOCH}_2\text{MgBr}$).

The structure assigned to the phenylated compound II was confirmed by its synthesis from the bromomagnesium enolate of acetomesitylene and benzalacetomesitylene.



The dimesitylpentadienolone (I) was made by condensing the bromomagnesium enolate of acetomesitylene with ethyl formate by a modification of the method of Fuson, Fugate and Fisher.¹ Under suitable conditions the intermediate hydroxy diketone VI could be isolated. The synthesis of this compound, it may be noted, is very similar to that of α,γ -dibenzoyl- α,γ -dibenzohydril- β -hydroxypropane reported by Kohler and Peterson.²

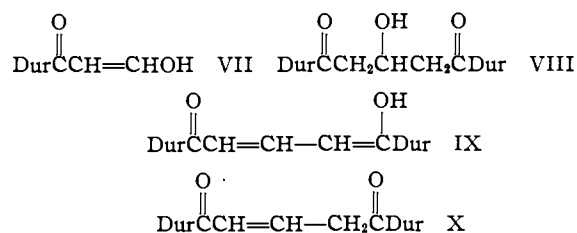
The dimesitylpentadienolone (I) could be made also by condensing the bromomagnesium enolate of acetomesitylene with the hydroxymethylene derivative of acetomesitylene. A mole of the magnesium compound serves to generate the enolate IVa,b which condenses with a second mole of the magnesium compound to yield the ion V corresponding to the hydroxy precursor VI of the observed product.



It is apparent from the principal resonance structures IVa,b of the enolate, a vinylog of the mesitoate ion, that the aldehyde carbon atom is the principal cationoid center.

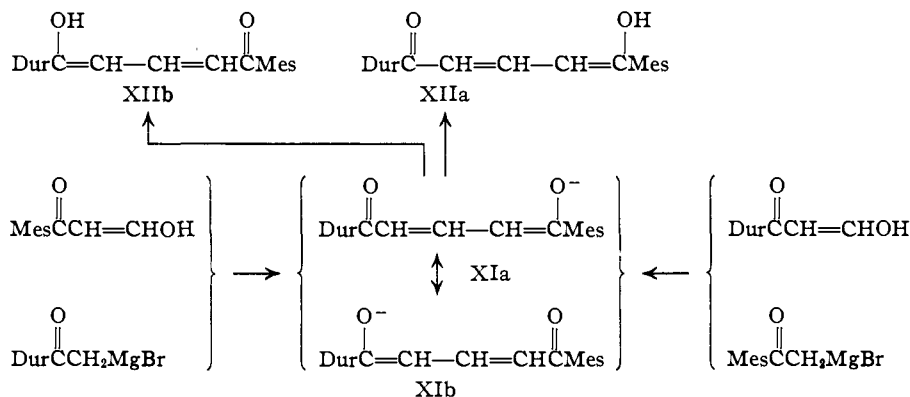
When acetodurene was employed the condensation with ethyl formate yielded the hydroxy methylene derivative VII, the hydroxydiketone VIII, or the didurylpentadienolone (IX), depending on the

procedure employed. Prolonged heating in petroleum ether caused the enol to ketonize; when the solution was allowed to cool, the yellow diketone X separated.



Condensation of the didurylpentadienolone with phenylmagnesium bromide gave 1,5-diduryl-3-phenyl-1,5-pentadione. When one mole of the Grignard reagent was employed and the addition was performed in the inverse manner the pentadienol was recovered unchanged.

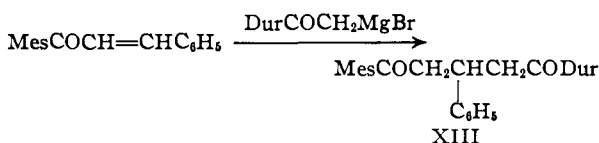
As the following chart indicates, the method of making the dimesityl and didurylpentadienolones was adapted to the preparation of keto enols of this type in which the two aryl radicals are different.



The durylmesityl enol was made in the two ways shown in the diagram.

Since the two isomeric enols XIIa and XIIb are derived from a common enolate XIa, b, it is not possible, without further information, to assign either structure to the product.

Treatment of the "unsymmetrical" dienolone XIIa,b with phenylmagnesium bromide produced 1-duryl-5-mesityl-3-phenyl-1,5-pentadione (XIII), the structure of which was established by its preparation from benzalacetomesitylene and the enolate of acetodurene.



Experimental³

1,5-Dimesityl-1,3-pentadien-1-ol-5-one (I).—A solution of 24.3 g. (0.15 mole) of acetomesitylene in 50 ml. of dry benzene was added dropwise, with stirring, to the Grignard reagent previously prepared from 16.4 g. of ethyl bromide and 3.7 g. of magnesium turnings in a mixture of 75 ml. of dry benzene and 25 ml. of dry ether. After the mixture had been boiled under reflux for one-half hour and cooled, a solution of 11.1 g. (0.15 mole) of ethyl formate in 40 ml.

(1) R. C. Fuson, W. O. Fugate and C. H. Fisher, *THIS JOURNAL*, **61**, 2302 (1939).

(2) E. P. Kohler and W. D. Peterson, *ibid.*, **65**, 1073 (1933).

(3) All melting points are uncorrected.

of benzene was added. The resulting clear solution was stirred at room temperature for one hour and boiled under reflux for an additional hour. When the reaction mixture was treated with an ice-cold, saturated solution of ammonium chloride an emulsion was produced which was broken by acidification with dilute hydrochloric acid. The organic layer was washed well with water and extracted with 10% sodium carbonate solution; the extract contained the hydroxymethyleneacetomesitylene, isolation of which is described below. The benzene solution was concentrated on the steam-bath and diluted with a large volume of low-boiling petroleum ether. After being allowed to stand in the ice-box overnight, the solution was found to have deposited a solid, which was collected on a filter and washed with petroleum ether; m.p. 152–156°, yield 2.48 g. (5%). One crystallization from 95% ethanol afforded the dimesitylpentadienolone as amber-colored, flat prisms melting at 159–159.5°. Further recrystallization of the dienolone did not change its melting point or color.

*Anal.*⁴ Calcd. for $C_{23}H_{26}O_2$: C, 82.60; H, 7.84. Found: C, 82.86; H, 7.89.

The infrared absorption spectrum⁵ of this compound contains a broad shoulder band in the region of 3000 cm^{-1} suggestive of a strongly bonded hydroxyl group. A broad, intense absorption band in the 1500–1600 cm^{-1} region is attributed to the conjugated, hindered carbonyl absorption. This band contains two small maxima at 1537 and 1585 cm^{-1} .

Presumably the pentadienolone was formed from the intermediate hydroxy diketone by the dehydrating action of the acid used in decomposing the Grignard reaction mixture. Isolation of the hydroxy compound was achieved in an experiment described below.

Hydroxymethyleneacetomesitylene.—The soda extract from the preceding experiment was carefully acidified with dilute hydrochloric acid. The liberated oil was taken up in ether, the solution shaken with saturated aqueous cupric acetate and the insoluble copper complex was collected on a filter; yield 11.0 g. (33%). The hydroxymethyleneacetomesitylene was isolated in sufficient purity for synthetic purposes merely by shaking an ethereal suspension of the copper complex with dilute hydrochloric acid. After the ether layer had been washed well with water and dried over anhydrous magnesium sulfate, the solvent was evaporated *in vacuo*.

1,5-Dimesityl-1,5-pentadiene-3-ol (VI).—The bromomagnesium enolate prepared from 0.20 mole of acetomesitylene was treated with a benzene solution of 0.10 mole of ethyl formate and the reaction was completed as described above. Decomposition with cold, very dilute hydrochloric acid was followed by extraction with sodium carbonate solution. Treatment of the concentrated benzene layer with low-boiling petroleum ether liberated the crude diketo alcohol as a white solid, m.p. 115–117°, yield 2.4 g. (7%). It crystallized from aqueous ethanol as white platelets, m.p. 118.5–119.5°.

Anal. Calcd. for $C_{23}H_{26}O_3$: C, 78.38; H, 8.01. Found: C, 78.65; H, 8.17.

The soda extract again afforded hydroxymethyleneacetomesitylene, isolated as its copper complex; yield 11.2 g. (50%).

The diketo alcohol was dissolved in a hot mixture of ethanol and concentrated hydrochloric acid (7:3). When the solution was cooled the dimesitylpentadienolone separated; yield 80%, m.p. 157.5–159°.

Reaction of the Bromomagnesium Enolate of Acetomesitylene with Ethyl Formate in a Molar Ratio of Three to One.—Treatment of the enolate, prepared from 0.15 mole of acetomesitylene, with 0.05 mole of ethyl formate produced 3.1 g. (19%) of the dimesitylpentadienolone (I), m.p. 157–159°. Only a trace (0.1 g.) of the copper complex of hydroxymethyleneacetomesitylene was obtained.

Reaction of the Bromomagnesium Enolate of Acetomesitylene with Hydroxymethyleneacetomesitylene.—The enolate was prepared from 15.6 g. of acetomesitylene, and the hydroxymethylene compound (6.1 g.) in 25 ml. of dry ben-

zene was slowly added to the Grignard mixture. The solution was boiled under reflux for 3 hours, cooled and decomposed with hydrochloric acid. The dimesitylpentadienolone crystallized from ethanol; yield 3.4 g. (32%), m.p. 156–157°.

The acetate of the dienolone (I) was made by heating a solution of 0.30 g. of the enol in 5 ml. of acetic anhydride under reflux for 2 hours. The excess acetic anhydride was decomposed with a large volume of ice-water and the solid was collected. It crystallized from 70% ethanol as faintly yellow needles; yield 0.22 g., m.p. 70–71°. It was recrystallized twice from 70% ethanol; m.p. 71–72°.

Anal. Calcd. for $C_{25}H_{28}O_3$: C, 79.75; H, 7.50. Found: C, 79.82; H, 7.57.

The infrared absorption spectrum has bands which may be attributed to a vinyl ester carbonyl group (1767 cm^{-1}) and to a hindered conjugated ketone group (1649 cm^{-1}) and indicates that the hydroxyl group is absent.

A small amount of the acetate, dissolved in 95% ethanol, was hydrolyzed by dissolving a small pellet of sodium metal in the alcoholic solution. The mixture was diluted with water and acidified with dilute hydrochloric acid. The product, after recrystallization, was identified as the original enol by its melting point (157–158°) and by a mixed melting point.

1,5-Dimesityl-3-phenyl-1,5-pentadiene (II).—To the enolate prepared from 3.24 g. of acetomesitylene was added dropwise, with stirring, a solution of 5.0 g. of benzalacetomesitylene in 10 ml. of ether. The mixture was boiled under reflux for one hour and worked up in the usual manner. The crude 1,5-dimesityl-3-phenyl-1,5-pentadiene was crystallized three times from 95% ethanol; yield 3.8 g. (46%), m.p. 138–139°.

Anal. Calcd. for $C_{29}H_{32}O_2$: C, 84.41; H, 7.82. Found: C, 84.25; H, 8.03.

Reaction of 1,5-Dimesityl-1,3-pentadien-1-ol-5-one with Phenylmagnesium Bromide.—To the Grignard reagent, prepared from 1.3 g. of bromobenzene and 0.2 g. of magnesium in 15 ml. of dry ether, was added dropwise, with stirring, a suspension of 1.3 g. of the enol in 50 ml. of benzene. After the addition was completed the mixture was boiled under reflux, with stirring, for one hour and decomposed with an ice-cold solution of ammonium chloride. Evaporation of the solvents left a residue which crystallized from 95% ethanol as fine, white needles; yield 0.68 g. (41%), m.p. 136.5–137.5°. A mixture of this material with the product obtained in the foregoing procedure melted at 138–139°.

1,5-Diduryl-1,5-pentadiene-3-ol (VIII).—A benzene solution of the enolate Grignard was prepared from 26.6 g. (0.15 mole) of acetodurene and an equivalent amount of ethylmagnesium bromide. To the cooled enolate mixture was added a solution of 11.1 g. (0.15 mole) of ethyl formate in ether and the solution was stirred at room temperature for 2 hours and finally at reflux temperature for one hour. The reaction mixture was cooled, decomposed with cold dilute hydrochloric acid and extracted with 10% sodium carbonate solution. Treatment of the concentrated organic layer with 200 ml. of low-boiling petroleum ether deposited the hydroxy diketone as a white solid. It was collected on a filter and the filtrate was preserved for the recovery of acetodurene. The solid diketone crystallized from 95% ethanol; yield 4.6 g. (8%), m.p. 118.5–120°. Three recrystallizations gave a product of analytical purity, m.p. 121–122°.

Anal. Calcd. for $C_{25}H_{32}O_3$: C, 78.91; H, 8.48. Found: C, 78.94; H, 8.37.

Hydroxymethyleneacetodurene.—Careful acidification of the soda extract from the preceding procedure gave hydroxymethyleneacetodurene as a white solid; yield 14.8 g. (48%). It was recrystallized three times from 50% ethanol; m.p. 90–91°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.43; H, 7.90. Found: C, 76.48; H, 7.99.

When this compound was recrystallized from ether the melting point was raised to 100–101°. Admixture with the low-melting material gave a sample melting at ca. 94–96°.

The cupric enolate of hydroxymethyleneacetodurene was prepared by shaking an ethereal solution of the hydroxy compound with saturated aqueous cupric acetate. The insoluble complex was collected and crystallized from carbon

(4) The microanalyses were carried out by Mrs. Katherine Pih, Miss Emily Davis and Mr. Joseph Nemeth.

(5) The authors are indebted to Miss Helena Miklas for the measurement and interpretation of the infrared spectra mentioned in this paper. All of the spectra were determined in Nujol mull.

tetrachloride; it formed finely-divided gray crystals, m.p. 246–247° dec.

Anal. Calcd. for $(C_{13}H_{15}O_2)_2Cu$: C, 66.43; H, 6.43. Found: C, 66.32; H, 6.59.

The ferric enolate of the hydroxymethylene compound was prepared by adding a 3% aqueous solution of ferric chloride to an equal volume of a concentrated alcohol solution of hydroxymethyleneacetodurene. After being allowed to stand for 10 minutes the orange solid was collected; it separated from a mixture of petroleum ether (b.p. 90–120°) and chloroform as a deep-orange micro-crystalline solid, m.p. ca. 295–300° dec.

Anal. Calcd. for $(C_{13}H_{15}O_2)_2Fe$: C, 70.37; H, 6.82; Fe, 8.39. Found: C, 70.11; H, 6.96; Fe as (Fe_2O_3) , 8.20.

1,5-Diduryl-1,3-pentadien-1-ol-5-one (IX).—The diduryl hydroxy diketone (m.p. 118.5–120°) was dissolved in a hot ethanol-hydrochloric acid mixture (7:3). The cooled solution afforded an excellent yield of the didurylpentadienolone, m.p. 160.5–161.5°.

Anal. Calcd. for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 83.03; H, 8.38.

The infrared absorption spectrum shows a broad shoulder band in the region of 3000 cm^{-1} , which may be attributed to the hydroxyl group. A broad band in the 1500–1600 cm^{-1} region containing a maximum at 1548 cm^{-1} and a shoulder at 1585 cm^{-1} is imputed to absorption by the conjugated, hindered ketone group.

The acetate of the pentadienolone was prepared by heating 0.2 g. of the enol with 5 ml. of acetic anhydride under reflux for one hour. The excess acetic anhydride was decomposed with water and the enol acetate was crystallized three times from 70% ethanol; m.p. 119–120°.

Anal. Calcd. for $C_{27}H_{32}O_2$: C, 80.17; H, 7.98. Found: C, 80.27; H, 8.04.

The infrared absorption spectrum has a maximum at 1764 cm^{-1} assignable to a vinyl ester carbonyl group and a band at 1653 cm^{-1} attributable to a conjugated, hindered carbonyl group.

Reaction of the Bromomagnesium Enolate of Acetodurene with Ethyl Formate. (a) In a Molar Ratio of Two to One.—The enolate, prepared from 0.20 mole of acetodurene, was treated with 0.10 mole of ethyl formate. The reaction afforded hydroxymethyleneacetodurene, isolated as its copper derivative, in 42% yield. This product was accompanied by a 10% yield of the crude didurylpentadienolone. The latter was crystallized from ethanolic hydrochloric acid; yield 7%, m.p. 159–160.5°.

(b) In a Molar Ratio of Three to One.—The enolate prepared from 0.15 mole of acetodurene was allowed to react with 0.05 mole of ethyl formate. The reaction was completed by prolonged boiling, under reflux, but a granular suspension remained. In other experiments in this series, utilizing lower reactant ratios, the reaction mixture consistently became clear upon the addition of the formate. The mixture was nevertheless manipulated in the prescribed manner and afforded relatively pure hydroxymethyleneacetodurene; yield 9.4 g. (92%), m.p. 98–99°. None of the expected didurylpentadienolone nor the corresponding diketo alcohol was isolated.

Reaction of the Bromomagnesium Enolate of Acetodurene with Hydroxymethyleneacetodurene.—A benzene solution of the enolate prepared from 10.6 g. (0.06 mole) of acetodurene was treated with a solution of 4.1 g. (0.02 mole) of hydroxymethyleneacetodurene in 50 ml. of warm benzene. The mixture was boiled under reflux for 3 hours, cooled and decomposed with cold, dilute hydrochloric acid. The concentrated organic layer was again treated with low-boiling petroleum ether and afforded 1.2 g. of a solid, m.p. 98–145°. This material, apparently the partially dehydrated diduryl hydroxy diketone, was crystallized from ethanolic hydrochloric acid to give the pure didurylpentadienolone; yield 0.9 g. (12%), m.p. 159.5–161°. Appreciable amounts of acetodurene were recovered from the petroleum ether liquors.

Inverse Reaction of Phenylmagnesium Bromide with 1,5-Diduryl-1,3-pentadien-1-ol-5-one. 1,5-Diduryl-3-phenyl-1,5-pentadiene.—The Grignard reagent prepared from 0.003 mole of bromobenzene was added, under a nitrogen atmosphere and with stirring, to a suspension of a molar equivalent amount of the pentadienolone in benzene the

resulting mixture was boiled under reflux with stirring, for one hour. Following hydrochloric acid decomposition the enol was recovered unchanged. When the molar ratio of phenylmagnesium bromide to enol was *two to one* the reaction afforded the phenylated diduryl pentadiene, which crystallized from ethanol; yield 0.64 g. (49%), m.p. 186–187.5°. Two recrystallizations gave fine white needles, m.p. 188–189°.

Anal. Calcd. for $C_{31}H_{36}O_2$: C, 84.48; H, 8.24. Found: C, 84.50; H, 8.21.

A mixed melting point determination showed this product to be identical with that obtained from the reaction of equimolar quantities of benzalacetodurene and the enolate Grignard reagent of acetodurene.

1,5-Diduryl-2-penten-1,5-dione (X).—A mixture of 0.5 g. of the enol and 25 ml. of petroleum ether (b.p. 90–120°) was boiled under reflux, in an atmosphere of nitrogen, for 6 hours. The yellow solution deposited the didurylpentenedione when cooled; m.p. 129–131°. The solid crystallized from high-boiling petroleum ether as tiny, nearly white flakes, m.p. 133–134°.

Anal. Calcd. for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.62; H, 8.37.

The infrared absorption spectrum has bands attributable to a hindered, conjugated carbonyl (1658 cm^{-1}) and a simple hindered carbonyl group (1691 cm^{-1}) and indicates that the hydroxyl group is absent.

Crystallization of the pentenedione from ethanol containing a trace of hydrochloric acid effected tautomerization to the pentadienolone, m.p. 161–162°. A mixed melting point with a known sample of the enol showed no depression.

The Durylmesitylpentadienolone (XIIa,b). Reaction of the Bromomagnesium Enolate of Acetodurene with Hydroxymethyleneacetomesitylene.—A solution of 4.3 g. of hydroxymethyleneacetomesitylene in 30 ml. of dry benzene was added rapidly to the enolate previously prepared from 12.4 g. of acetodurene. The reaction mixture was boiled under reflux, with stirring, for a period of 4 hours, cooled and decomposed with hydrochloric acid. The isolation procedure was that previously described; the solid product, obtained in 5% yield, crystallized from 70% ethanol as light-amber needles, m.p. 134–135°.

Anal. Calcd. for $C_{24}H_{28}O_2$: C, 82.71; H, 8.10. Found: C, 82.92; H, 8.05.

The infrared absorption spectrum shows a broad absorption band in the region of 3000 cm^{-1} associated with a hydrogen bonded hydroxyl group and a broad band with a maximum at 1589 cm^{-1} and a shoulder at 1550 cm^{-1} imputed to the conjugated carbonyl group.

Reaction of the Bromomagnesium Enolate of Acetomesitylene with Hydroxymethyleneacetodurene.—The enolate, prepared from 9.7 g. of acetomesitylene, was treated with a warm benzene solution of 4.1 g. of hydroxymethyleneacetodurene and the reaction was completed in the usual manner. The crude product crystallized from 70% ethanol; yield 0.63 g. (9%), m.p. 133–134°. A mixed melting point with the duryl mesityl pentadienolone from the preceding experiment showed no depression.

1-Duryl-3-phenyl-5-mesityl-1,5-pentadiene (XIII).—A solution of 5.0 g. of benzalacetomesitylene in 20 ml. of ether was added to the enolate prepared from 3.5 g. of acetodurene. The mixture was boiled under reflux, with stirring, for one hour, cooled and decomposed with dilute hydrochloric acid. White needles separated in the organic phase; yield 5.7 g. (66%), m.p. 165–167°. The diketone was recrystallized from a large volume of ethanol; m.p. 167.5–168.5°.

Anal. Calcd. for $C_{30}H_{34}O_2$: C, 84.47; H, 8.03. Found: C, 84.22; H, 8.24.

Reaction of Phenylmagnesium Bromide with the Duryl Mesityl Pentadienolone.—To the Grignard reagent prepared from 0.63 g. of bromobenzene was added a suspension of 0.50 g. of the enol in 10 ml. of benzene. The mixture was boiled under reflux for one hour, cooled and decomposed with acid; the product was crystallized three times from ethanol; m.p. 166–167°. A mixture with a sample of the phenylated diketone from the preceding experiment melted at 167.5–168.5°.