solution of silver nitrate. A sample of methylenecyclohexene dibromide, b.p. 112° (16 mm.), n^{20}_D 1.5442, was analyzed. The properties previously reported[20] are b.p. 121.5–123° (27 mm.), d_0 1.7156.

Anal. Calcd. for $C_7H_{12}Br_2$: C, 32.85; H, 4.73. Found: C, 33.34; H, 4.77.

The monobromide reacted immediately with alcoholic silver nitrate to give a copious precipitate and also decolorized bromine in carbon tetrachloride solution and potassium permanganate solution. A heart cut, b.p. 80° (16 mm.), n^{25}_D 1.5267, was analyzed.

Anal. Calcd. for $C_7H_{11}Br$: C, 48.02; H, 6.33. Found: C, 47.42; H, 6.40.

MINNEAPOLIS 14, MINNESOTA

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF A. BOAKE, ROBERTS AND COMPANY LIMITED]

The Reactions of Diketene with Ketones[1]

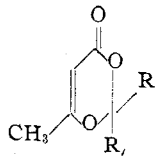
BY MICHAEL F. CARROLL AND ALFRED R. BADER[2]

RECEIVED JUNE 1, 1953

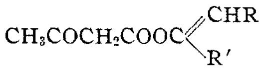
The acid-catalyzed reactions of diketene with ketones yield 2,2-disubstituted-4-methyl-6-keto-1,3-dioxenes (I), many reactions of which parallel those of diketene.

Although the preparation of ketene and diketene in acetone is a commercial process, the reaction of diketene has not been investigated in any detail.[3] When acetone and diketene are heated on the steam-bath with a catalytic amount of *p*-toluenesulfonic acid, a crystalline solid, $C_7H_{10}O_3$, melting at 12–13°, can be isolated in 91% yield. Reactions with other unhindered ketones proceed similarly, and pure adducts are obtained from methyl ethyl ketone, acetophenone and dibenzyl ketone. Ketones which are more hindered sterically react more sluggishly and diisobutyl ketone, benzophenone and also acetoacetates do not appear to react at all.

Three structures, I, II and III were considered.

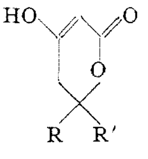


I



$$CH_3COCH_2COOC{\overset{CHR}{\underset{R'}{<}}}$$

II

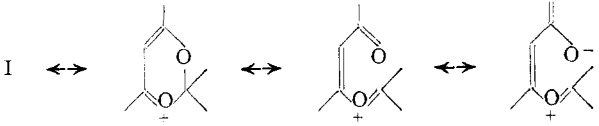


III

That of the enol acetoacetate II was rejected because of the adducts' non-reactivity with carbonyl reagents and because the adducts' ultraviolet spectra are inconsistent with II. Acetoacetates, even of complex alcohols, are known to react readily with carbonyl reagents[4] whereas the adducts do not. Intensities of absorption maxima of acetoacetates increase sharply on passage to non-polar solvents because chelated enols are favored by non-solvating media. The adducts' ultraviolet spectra show identical intensities in water, ethanol and isoöctane.[5] Furthermore the spectra of acetoacetates of the enols of acetophenone and dibenzyl ketone would be the composite of the spectra of substituted styrenes and acetoacetates. The spectra of the adducts of these ketones, however, are very similar to that of the acetone adduct.

The enol III can be considered as the lactone of an aldol condensation product of acetoacetic acid and ketones. Similar 4-hydroxy-5,6-dihydro-2-pyrones have been prepared as analogs of the enol lactone form of auxin b. The methyl analog[6] (III, R = –CH$_3$, R′ = –H) reacts readily with dinitrophenylhydrazine and semicarbazide, and absorbs in the ultraviolet at somewhat lower wave lengths than do the diketene adducts. The phenyl analog[7] (III, R = –C$_6$H$_5$, R′ = –H) also reacts with semicarbazide and in contrast to the spectra of the diketene adducts shows in the infrared a strong enolic hydroxyl band at *ca.* 4.0 μ and no carbonyl band below 6.1 μ.

2,2-Disubstituted-4-methyl-6-keto-1,3-dioxenes (I) should be unstable in aqueous acid and alkali, should not react with carbonyl reagents and should react as do diketene and acetoacetic acid with alcohols and amines. The adducts' ultraviolet and infrared spectra are in accord with structure I. Their ultraviolet maxima in ethanol at 247–252 mμ are at longer wave lengths than those of β-alkoxycrotonates,[8] an exaltation attributable to resonance contributions of structures Ia ↔ Ib ↔ Ic analogous to the exaltation of cyclohexadiene.[9]



Ia Ib Ic

Figure 1 shows the infrared spectra of the acetone and acetophenone adducts. The pronounced associated hydroxyl band present in the spectra of cyclic 1,3-diketones such as dimedone at 3.4 μ, and in six-membered enol lactones such as III at *ca.* 4.0 μ is absent, and the carbonyl bands, at *ca.* 5.8 μ, are at significantly lower wave lengths than the carbonyl band of III. Thus we favor structure I for these diketene ketone adducts.

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(1) For a preliminary communication, *cf.* THIS JOURNAL, **74**, 6305 (1952).

(2) The Research Laboratories, The Pittsburgh Plate Glass Co., Milwaukee, Wisconsin.

(3) In the reaction of ketene with acetone, which is catalyzed by zinc chloride, R. F. Naylor (*J. Chem. Soc.*, 244 (1945)), observed the formation in low yield of a product, $C_7H_{10}O_3$, thought to be isopropenyl acetoacetate. This may have been the diketene–acetone adduct here described.

(4) M. F. Carroll, *J. Applied Chem.*, 443 (1951).

(5) The log ε's reported in ref. 3 were 3.93 in water and 4.0 in cyclohexane. Our values for the acetone adduct are 3.94 in water and 3.93 in isoöctane.

(6) E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1419 (1949).

(7) E. B. Reid and W. R. Ruby, THIS JOURNAL, **73**, 1054 (1951).

(8) K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

(9) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939).

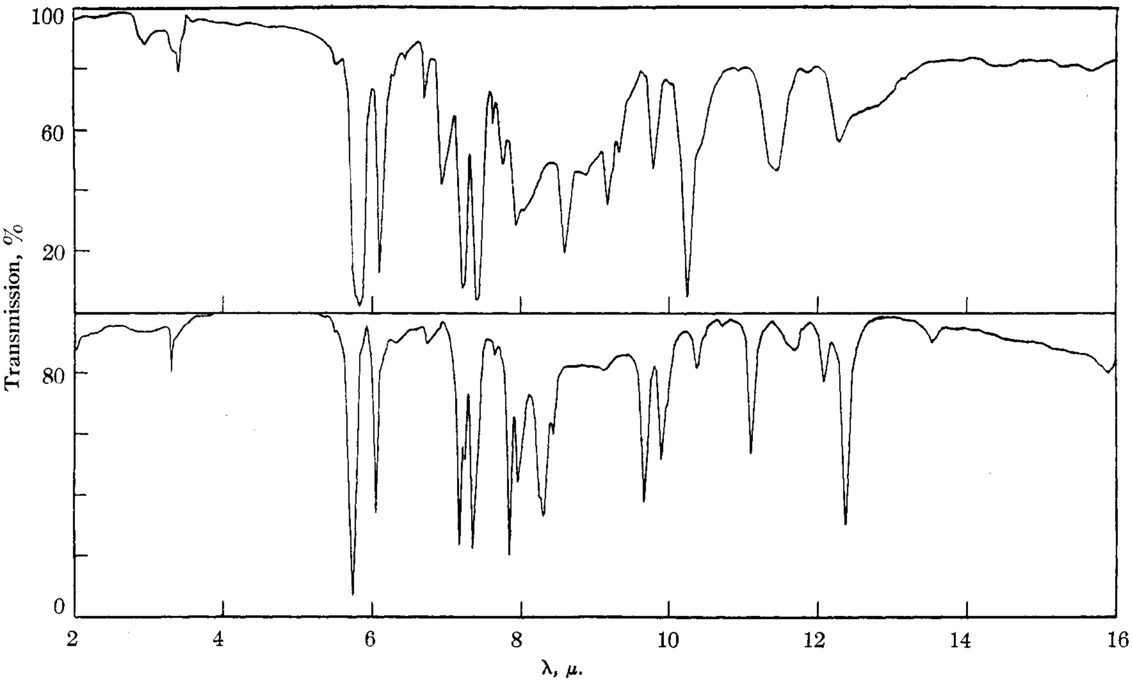
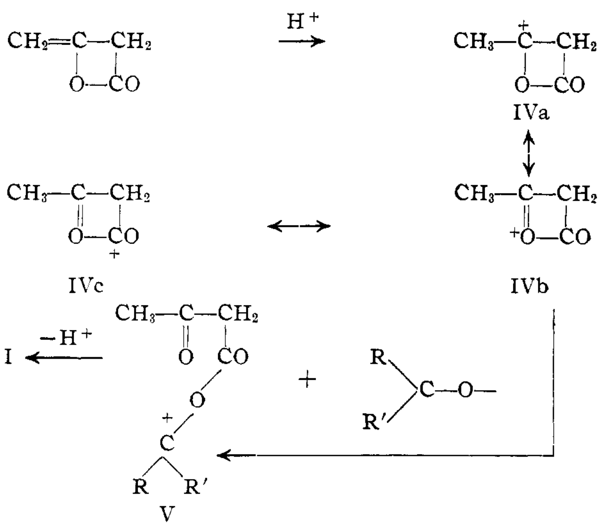
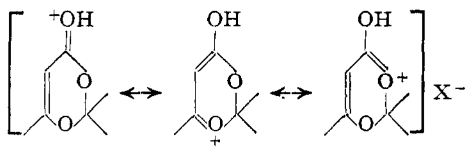


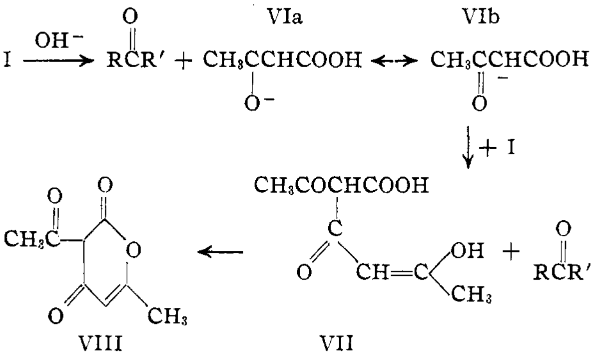
Fig. 1.—Infrared absorption spectra of the acetophenone–diketene adduct, 2,4-dimethyl-2-phenyl-6-keto-1,3-dioxene (upper) in chloroform solution, and of the acetone–diketene adduct, 2,2,4-trimethyl-6-keto-1,3-dioxene (lower) in carbon disulfide solution.

The mechanism of this acid-catalyzed reaction might be pictured as the attack on the carbonyl of the ketone by the resonant cation IV formed by addition of a proton to diketene, followed by cyclization of V to I.



Diketene, acetoacetates and I are all fairly stable to anhydrous acids[10]; with alkali all yield dehydracetic acid and resins, the reaction rates being in the order diketene >> I > acetoacetates; and all react with alcohols and aniline to yield acetoacetates and acetoacetanilide, respectively. The base-catalyzed formation of dehydracetic acid VIII from I can be rationalized by assuming initial ring opening of I by hydroxide ion followed by a nucleophilic attack of the resultant resonant anion VI on another molecule of I, and lactonization of the product VII.





Dehydracetic acid and resins are also formed by the prolonged action of acids on the adducts I and on diketene, and the latter also decomposes to ketene. Thus in the acid-catalyzed formation of I, it is accompanied by dehydracetic acid, ketene, and isopropenyl acetate from the reaction of ketene with acetone.

The adducts can be prepared easily and economically, and they are pleasant smelling, and quite stable in the absence of alkali. They may conveniently be used in place of diketene in many reactions.

Experimental

2,2,4-Trimethyl-6-keto-1,3-dioxene.—A mixture of dry acetone (100 cc.), diketene (100 cc., 109 g., 1.3 moles) and *p*-toluenesulfonic acid (0.5 g.) was refluxed for 3 hours, when the odor of diketene had disappeared. Excess acetone

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[10] I is considerably more stable to acids than are ordinary acetals A proton probably adds to the carbonyl of I to give a salt stabilized by considerable resonance.

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^{20}_{D} 1.4636, d^{20}_{4} 1.0879[11]; $\lambda_{\max.}^{\text{water}}$ 252.5 mμ (log ε 3.94); $\lambda_{\max.}^{\text{EtOH}}$ 247.5 mμ (log ε 3.92); $\lambda_{\max.}^{\text{isoöctane}}$ 239.0 mμ (log ε 3.93).

Anal.[12] Calcd. for $C_7H_{10}O_3$: 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^{20}_{D} 1.4590–1.4610, contained only traces of acetone, easily removed by water washing, and the later fractions, n^{20}_{D} 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^{20}_{D} 1.4633, d^{20}_{4} 1.065.

Anal. Calcd. for $C_8H_{12}O_3$: 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°. $\lambda_{\max.}^{\text{EtOH}}$ 247.5 mμ (log ε 3.86); $\lambda_{\max.}^{\text{isoöctane}}$ 240.0 mμ (log ε 3.84).

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.21; H, 5.80. Kuhn-Roth[13] C–CH_3 det.: Calcd. for 1 C–CH_3: 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*-toluenesulfonic acid, and crystallized from benzene melts at 104–105°; $\lambda_{\max.}^{\text{EtOH}}$ 252.5 mμ (log ε 3.77); $\lambda_{\max.}^{\text{isoöctane}}$ 246.0 mμ (log ε 3.77).

Anal. Calcd. for $C_{19}H_{18}O_3$: 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^{20}_{D} 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 acetoacetate**[14] 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.

LONDON, ENGLAND

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[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.

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

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

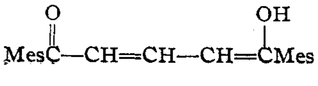
1,5-Diarylpentadienolonates

BY REYNOLD C. FUSON AND L. RUSSELL MELBY

RECEIVED JUNE 1, 1953

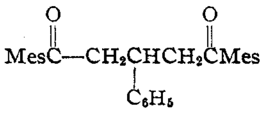
Three 1,5-diaryl-1,3-pentadien-1-ol-5-ones have been prepared in which the aryl radicals are mesityl or duryl. The method of synthesis involves the condensation of the bromomagnesium enolates of acetomesitylene and of acetodurene with the enolates corresponding to the hydroxymethylene derivatives of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



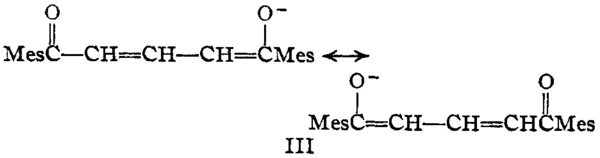
$$\text{Mes}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH=CH—CH=}\overset{\overset{\displaystyle OH}{|}}{C}\text{Mes}$$

I



$$\text{Mes}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_2\underset{\underset{\displaystyle C_6H_5}{|}}{C}HCH_2\overset{\overset{\displaystyle O}{\|}}{C}\text{Mes}$$

II



$$\text{Mes}\overset{\overset{\displaystyle O}{\|}}{C}\text{—CH=CH—CH=}\overset{\overset{\displaystyle O^-}{|}}{C}\text{Mes} \longleftrightarrow \text{Mes}\overset{\overset{\displaystyle O^-}{|}}{C}\text{=CH—CH=CH}\overset{\overset{\displaystyle O}{\|}}{C}\text{Mes}$$

III