Anal. Calcd for $C_6H_6O_2$: C, 65.44; H, 5.49. Found: C, 65.03; H, 5.43.

Registry No.—If, 13942-37-5; Ig, 14001-84-4; anisic acid, 100-09-4; IIa, 13942-38-6; IId, 13942-39-7; IIe, 13942-40-0; IIf, 13942-41-1; IIg, 13942-42-2; IIi, 13942-43-3; IIk, 13942-44-4; IIl, 13942-45-5; IIm, 13942-46-6; IIn, 13942-47-7; IIo, 13942-48-8; IIIa, 13942-49-9; IIIa′, 13942-50-2; IIIc, 13942-51-3; IIId, 13942-52-4; IVb, 13942-53-5; Vh, 13942-54-6; Vi, 14001-85-5; Vk, 13942-55-7; Vl, 13942-56-8; Vm, 13942-57-9; Vn, 13942-58-0; Vo, 13942-59-1; VIh, 6362-62-5; VIh oxime, 13942-61-5; VIi, 7147-41-3; VIl, 13942-63-7; VIm, 13942-64-8; VIn, 13942-65-9; VIIh, 156-06-9; VIIi, 4834-67-7; hydrogen peroxide, 7722-84-1.

Acknowledgment.—The authors wish to express their sincere thanks to Dr. Taro Hayashi and Dr. Tatsuo Takeshima for their kind advice.

The Base-Catalyzed Intermolecular Condensation of α,β-Unsaturated Ketones. Condensation of Benzaldehyde with 2-Butanone to Diketones $C_{22}H_{24}O_2$ and $C_{29}H_{28}O_2$

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Two new compounds derived by base-catalyzed (ethanolic sodium ethoxide) condensation of benzaldehyde and 2-butanone are described. Diketone $C_{22}H_{24}O_2$ is obtained slowly in low yield by self-condensation of styryl ethyl ketone and shown to be 3,5-diphenyl-2-methyl-4-propionylcyclohexan-1-one (**7**). Diketone $C_{29}H_{28}O_2$ is 4-(2-benzalpropionyl)-3,5-diphenyl-2-methylcyclohexan-1-one (**12**), obtained readily in 21% yield by condensation of styryl ethyl ketone with 1,5-diphenyl-2-methyl-1,4-pentadien-3-one. Spectral and chemical evidence is presented to support the structural assignments. Reactions of styryl ethyl ketone are compared with results of other workers on condensation reactions of benzaldehyde with 2-butanone and our previous findings on intermolecular self-condensation of other styryl alkyl ketones.

Many investigators have examined the reaction of benzaldehyde with 2-butanone in basic and acidic media. Several products have been reported. This report describes two new products derived from benzaldehyde and 2-butanone—diketones $C_{22}H_{24}O_2$ and $C_{29}H_{28}O_2$.

Products derived from one molecule each of benzaldehyde and 2-butanone include the aldol condensation ketols **1** and **2**[2] and their dehydration products, the corresponding α,β-unsaturated ketones **3** and **4**.[2,3] Acid catalysts favor **4**.[3a,m,4] Ketol formation (**1**, **2**) is favored by mild basic catalysis at low temperature.[2]

$C_6H_5CHOHCH_2COC_2H_5$ **1**

$C_6H_5CHOHCH(CH_3)COCH_3$ **2**

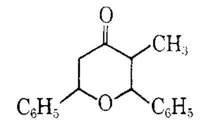
$C_6H_5CH{=}CHCOC_2H_5$ **3**

$C_6H_5CH{=}C(CH_3)COCH_3$ **4**

The distyryl ketone (**5**) has previously been prepared by hydrogen chloride catalyzed condensation of benzaldehyde with 2-butanone or ketone **4**.[3i] Its preparation from benzaldehyde and 2-butanone by base catalysis (aqueous ethanolic sodium hydroxide) is described in the present work.[5] The mono and bis-β-ketols corresponding to **5** have not been prepared. Base catalysis (aqueous or aqueous ethanolic sodium hydroxide) can produce the tetrahydro-1,4-pyrone **6** from benzaldehyde and 2-butanone,[3a,d,6] or from benzaldehyde and styryl ethyl ketone (**3**).[3d,6]

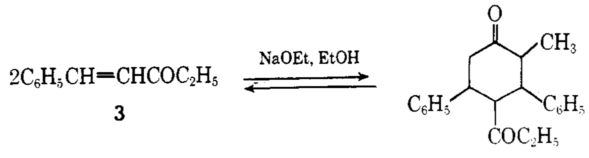
$C_6H_5CH{=}CHCOC(CH_3){=}CHC_6H_5$

5



6

Condensation products derived from two benzaldehyde and two 2-butanone molecules have not been described previously. Procedures (ethanolic sodium ethoxide or sodium hydroxide, 25°, 1–2 days) which readily effected self-condensation of certain styryl alkyl ketones ($ArCH{=}CHCOCH_2R$ with Ar = phenyl or phenyl with electron-releasing substituents, R = alkyl except CH_3) to cyclic diketone dimers (like **7**)[7] failed with styryl ethyl ketone itself. Diketone **7** forms extremely slowly from **3**; a 1% yield of **7** resulted only after the reaction mixture had been stored at −15° for *ca.* 3 years.



3 **7**

The slow step in formation of **7** is believed to involve Michael cyclization of the anion of the intermediate

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(1) Deceased.

(2) (a) H. Midorikawa, *Bull. Chem. Soc. Japan*, **27**, 131 (1954); *Chem. Abstr.*, **50**, 244 (1956); (b) M. Stiles, D. Wolf, and G. V. Hudson, *J. Am. Chem. Soc.*, **81**, 628 (1959).

(3) (a) C. Harries and G. H. Müller, *Chem. Ber.*, **35**, 966 (1902); (b) K. v. Auwers and H. Voss, *ibid.*, **42**, 4411 (1909); (c) K. von Auwers, *ibid.*, **45**, 2764 (1912); (d) H. Ryan and A. Devine, *Proc. Roy. Irish Acad.*, **32**, 208 (1916); *Chem. Abstr.*, **10**, 1850 (1916); (e) M. T. Bogert and D. Davidson, *J. Am. Chem. Soc.*, **54**, 334 (1932); (f) G. Massara and A. DiLeo, *Gazz. Chim. Ital.*, **63**, 199 (1933); (g) G. Massara, *ibid.*, **67**, 440 (1937); (h) H. Haeussler and C. Brugger, *Chem. Ber.*, **77B**, 152 (1944); (i) M. Métayer and N. Epinay, *Compt. Rend.*, **226**, 1095 (1948); (j) H. Haeussler and W. Schacht, *Chem. Ber.*, **83**, 129 (1950); (k) M. E. Egorova and M. A. Abramova, *Zh. Prikl. Khim.*, **24**, 1098 (1951); *Chem. Abstr.*, **46**, 7538 (1952); (l) M. G. J. Beets and H. van Essen, *Rec. Trav. Chim.*, **77**, 1138 (1958); (m) M. E. Kronenberg and E. Havinga, *ibid.*, **84**, 17 (1965); M. E. Kronenberg and E. Havinga, to be published. We are indebted to Professor Havinga and Dr. Kronenberg for providing us with their data prior to publication.

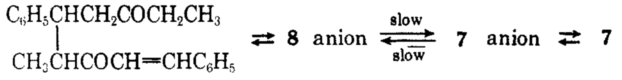
(4) (a) J. D. Gettler and L. P. Hammett, *J. Am. Chem. Soc.*, **65**, 1824 (1943); (b) D. S. Noyce and L. R. Snyder, *ibid.*, **81**, 620 (1959); (c) D. S. Noyce and W. L. Reed, *ibid.*, **81**, 624 (1959).

(5) *Cf.* C. R. Conard and M. A. Dolliver, *Org. Syn.*, **2**, 167 (1943).

(6) F. R. Japp and W. Maitland, *J. Chem. Soc.*, **85**, 1488 (1904).

(7) A. T. Nielsen and H. J. Dubin, *J. Org. Chem.*, **28**, 2120 (1963).

acyclic diketone **8**.[8,9] (Proton transfers involving **7** and **8** and their respective anions are believed to be rapid relative to the Michael cyclization[8]).



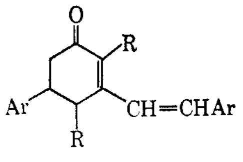
$$\begin{matrix} C_6H_5CHCH_2COCH_2CH_3 \\ | \\ CH_3CHCOCH{=}CHC_6H_5 \end{matrix} \rightleftarrows \textbf{8 anion} \underset{\text{slow}}{\overset{\text{slow}}{\rightleftarrows}} \textbf{7 anion} \rightleftarrows \textbf{7}$$

8

Alternatively, a slow, rate-limiting Michael addition of **3** anion to **3** (to form **8** anion) appears less likely since higher homologs of **8** form cyclic dimers so readily.[7] Also, certain phenyl-substituted derivatives of **8** are known intermediates in an intramolecular aldol condensation (see below).

Retrogression of **7** to **8** occurs slowly. In 80% ethanolic sodium hydroxide (0.5 *N*) at 25° a 10^{-4} *M* solution of **7** remained unchanged for 67 hr as evidenced by the stable ultraviolet spectrum. The strong π–π^* band of the cinnamoyl group in **3** and **8** did not appear, and the characteristic phenyl absorption bands of **7** remained with undiminished intensity. A sample of **7** in ethanolic sodium ethoxide heated under reflux for 3.5 hr was recovered unchanged (80% recovery). These preliminary data do not permit an evaluation of the equilibrium constant for **7** anion $\rightleftarrows$ **8** anion. The present evidence suggests that at equilibrium (very slowly attained) **8** and **3** are favored over **7**, and that the position of these equilibria, rather than the slow rate of formation of **7**, is responsible for the low yield of **7**. A low reaction temperature, such as that employed, would favor **7** in an exothermic equilibrium process.[7]

An intramolecular aldol condensation of **8** to a cyclic unsaturated ketone **9** (Ar = C_6H_5, R = CH_3) was not observed. Such products have been obtained from certain suitably substituted styryl methyl and styryl ethyl ketones (**9**, R = H, CH_3; Ar = 2-$CH_3OC_6H_4$; 2,3-, 2,5-, and 3,4-$(CH_3O)_2C_6H_3$; and 4-$(CH_3)_2NC_6H_4$).[10-12]



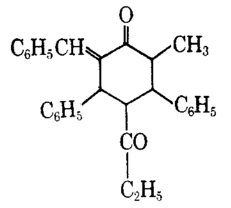
9

The formation of **7** from **3** is the first example of intermolecular self-condensation of any styryl ethyl ketone to a product other than **9**. One should conclude that the slow rate of formation of **7** in very low yield under unusual conditions, affirms, rather than negates, the generalization that styryl alkyl ketones, $ArCH{=}CHCOCH_2R$, lead to homologs of **7** when R is larger than methyl, and to **9** when R = H or CH_3.[12]

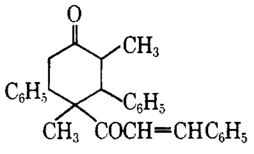
Chemical and physical properties of **7** (colorless needles, mp 190–191°) are like those of other styryl alkyl ketone dimers obtained previously.[7] The ultraviolet spectrum reveals only phenyl absorption of appropriate intensity. In the infrared spectrum unconjugated carbonyl absorption appears as a doublet at 1725 and 1700 cm^{-1} (potassium bromide). The nmr spectrum revealed characteristic ethyl group peaks and a methyl doublet. Diketone **7** was also obtained indirectly in another reaction sequence discussed below. Chemical evidence for its structure follows that discussion.

A product derived from three benzaldehyde and two 2-butanone molecules has been obtained for the first time in the present work: $C_{29}H_{28}O_2$, colorless prisms, mp 206.5–207.5°. It was first isolated as a product of attempted preparation of styryl ethyl ketone dimer **7**, employing the procedure which readily effected dimerizations of other styryl alkyl ketones (ethanolic sodium ethoxide, 25°, 1–2 days). The yield of this material was only 0.5% by this procedure with the customary 1:1 molar ratio of benzaldehyde to 2-butanone. However, the yield was increased to 6% when the molar ratio of aldehyde to ketone was increased to 3:2. A higher ratio of aldehyde to ketone did not improve the yield and led to much Cannizzaro reaction of the excess benzaldehyde.

Spectral properties of $C_{29}H_{28}O_2$ indicate a diketone having one conjugated and one nonconjugated carbonyl group, ν_{KBr} 1650, 1720 cm^{-1}; hydroxyl absorption bands were absent. Characteristic styryl alkyl ketone absorption is observed in the ultraviolet spectrum, λ_{max}^{EtOH} 286.5 mμ (ϵ 13,700).[13] These preliminary data and our previous findings suggest structures **10**–**12** as possible for the new product. The nmr spectrum of



10



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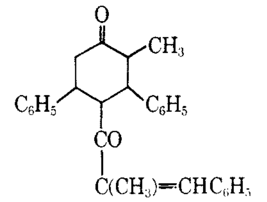

12

$C_{29}H_{28}O_2$ supports structure **12**; measurement in deuteriochloroform reveals 15 phenyl protons centered at τ 2.80; the side-chain methyl group attached to an olefinic double bond appears as a singlet at 8.70 and the ring-substituted methyl as a doublet at 9.10; the vinyl side-chain proton appears as a singlet at 3.4; the remaining ring protons appear as a complex multiple of five protons centered at 6.95 and a triplet (one proton) at 5.80.

Hydrogenation of **12** (platinum, ethanol, 40–50 psi) led to reduction of the ring carbonyl group, rather than the olefinic double bond of the side chain, to produce ketol **13** which retains the conjugated carbonyl group at

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(8) R. P. Bell, "The Proton in Chemistry," pp 109–123, Cornell University Press, Ithaca, N. Y., 1959.

(9) A homolog of **8** (CH_3 = *i*-C_3H_7) has been isolated from $C_6H_5CH{=}CHCOCH_2CH(CH_3)_2$ under similar reaction conditions; unpublished work.

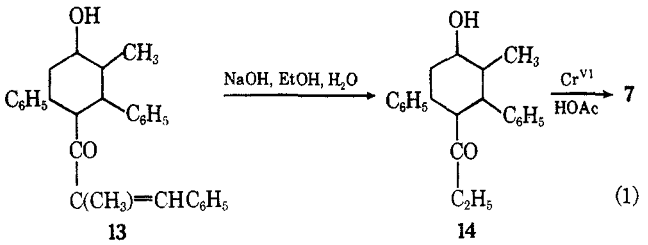
(10) R. Dickinson, I. M. Heilbron, and F. Irving, *J. Chem. Soc.*, 1888 (1927).

(11) C. V. Gheorghiu and B. Arwentiew, *Bull. Soc. Chim. France*, (4) **47**, 195 (1930).

(12) Spectral data support structure **9**: A. T. Nielsen and coworkers, unpublished results.

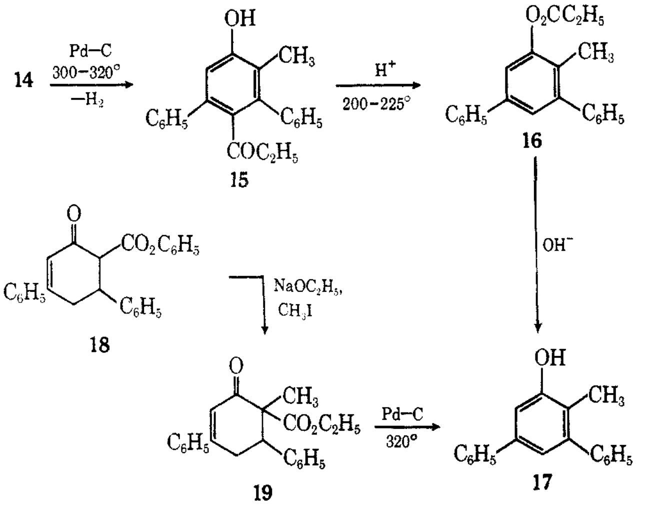
(13) (a) P. Yates, N. Yoda, W. Brown, and B. Mann [*J. Am. Chem. Soc.*, **80**, 202 (1958)] give $C_6H_5CH{=}C(CH_3)COC_2H_5$ λ_{max}^{EtOH} 277 mμ, ϵ_{max} 18,700. (b) $(CH_3)_2CHCH_2COCH{=}CHC_6H_5$ λ_{max}^{EtOH} 289 mμ, ϵ_{max} 19,400 (this laboratory. (c) H. O. House and R. L. Wasson [*J. Am. Chem. Soc.*, **78**, 4394 (1956)] give α-benzalcyclohexanone λ_{max}^{EtOH} 223 mμ (ϵ 6,700) and 290 mμ (ϵ 16,200).

1650 cm^{-1}, λ_{max}^{EtOH} 284 mμ (ε 13,900). Retroaldol cleavage of ketol **13** led to ketol **14** and benzaldehyde (isolated as its 2,4-dinitrophenylhydrazone). Chromic acid oxidation of **14** produced diketone **7**, identical with the diketone obtained by self-condensation of styryl ethyl ketone (eq 1).



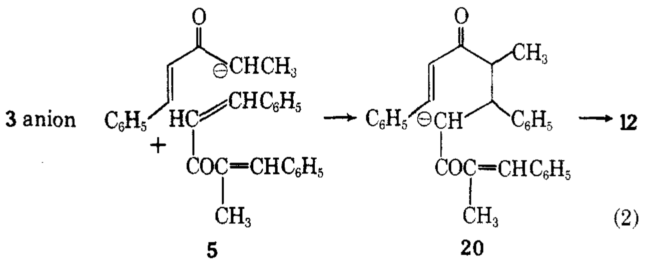
13 **14** (1)

Dehydrogenation of **14** with palladium–charcoal gave 3,5-diphenyl-2-methyl-4-propionylphenol (**15**). Heating **15** with camphor sulfonic acid effected a reverse Fries rearrangement to the propionic ester **16**, not isolated. Saponification of **16** led to propionic acid and 3,5-diphenyl-2-methylphenol (**17**), identical with an authentic sample synthesized from known keto ester **18**[14–16] by the sequence **18** → **19** → **17**. Direct dehydrogenation and decarbethoxylation of the methyl keto ester **19** to yield **17** proceeded readily on heating with palladium–charcoal; **17** was also prepared by dehydrogenation of 3,5-diphenyl-6-methyl-2-cyclohexen-1-one. It was possible to prepare phenol **17** directly from diketone **12** by heating with palladium–charcoal, followed by saponification; intermediates corresponding to **15** and **16** [$C_2H_5CO{=}C_6H_5CH{=}C(CH_3)CO$], and product α-methylcinnamic acid were not isolated.



15 **16** **18** **19** **17**

The reaction mechanism by which condensation product **12** is formed was examined in terms of participating intermediates. It was established that styryl ethyl ketone (**3**) and the distyryl ketone **5** were involved since they combine under the reaction conditions to produce **12** in an improved yield (21%). Yields of this order (13–22%) are obtained by self-condensation of styryl alkyl ketones to homologs of **7**.[7] The reaction is believed to involve an intermolecular Michael addition of **3** anion to **5** on the unsubstituted styryl group to form **20** (eq 2). (Addition on the other, methyl-substituted, styryl group would ultimately produce diketone **11**.) Finally, an intromolecular Michael addition in **20** yields **12**. The reaction sequence to form **12** does not involve an aldol condensation of benzaldehyde with diketone **7** since no **12** is produced from these substances under the reaction conditions. Furthermore, as noted above, no **7** is produced from styryl ethyl ketone under the usual reaction conditions whereby **12** is formed. These findings also argue against structure **10** for $C_{29}H_{28}O_2$.



5 **20** (2)

Reactions of styryl ethyl ketone examined in the present work agree with our previous conclusions on base-catalyzed intermolecular condensations of homologous styryl alkyl ketones, $C_6H_5CH{=}CHCOCH_2R$. The initial step is a Michael addition to an acyclic 1,5-diketone anion (**8** anion, **20**). Ring closure of the acyclic diketone anion is favored by large alkyl (R) substituents and disfavored by smaller groups such as hydrogen or methyl. Thus, styryl propyl ketone readily leads to a cyclic diketone (**7**, $CH_3{=}C_2H_5$, 17% yield[7]) and **20** cyclizes to **12**, but cyclization of **8** to **7** is not favored.[7,17]

Formation of diketone **12** by base-catalyzed condensation of benzaldehyde with 2-butanone is a unique reaction. No other product of this type has been previously reported although over 150 aldol condensations of benzaldehyde and substituted benzaldehydes with dialkyl ketones, RCH_2COCH_2R', have been described.[18] Explanation of this fact follows from our previous and present findings,[7,17] and the known behavior of ArCHO and RCH_2COCH_2R' in *base-catalyzed* aldol condensations,[18] which may be summarized as follows: (1) styryl alkyl ketones, $RCH_2COCH{=}CHAr$, are readily obtained by aldol condensation from methyl alkyl ketones, RCH_2COCH_3, by condensation on the methyl group; (2) dialkyl ketones, RCH_2COCH_2R' (R,R' = alkyl), condense less readily and yields of styryl alkyl ketone **21** (R' = alkyl) are very low, particularly when R' is larger than methyl; (3) distyryl ketones (**22**) form with particular difficulty with basic catalyst, except from acetone (**22**, R,R' = H); (4) as shown by the structure of **12**, formation of acyclic diketone **23** is favored only when R' is H; (5) cyclization of **23** to **24** is favored when R = alkyl and R' = H; (6) formation of **23** and **24** by Michael additions should be favored by electron-releasing substituents in Ar, by analogy with the behavior of **8**.[7]

Formation of **24** directly from reactants ArCHO and RCH_2COCH_2R' evidently becomes possible only when R = CH_3 and R' = H, *i.e.*, with 2-butanone. However, the present work demonstrates that improved yields of **24** can be realized by employing preformed

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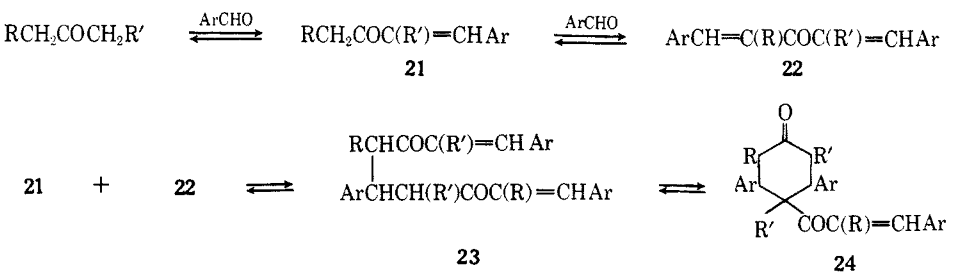
[14] E. Knoevenagel and H. Schmidt, *Ann.*, **281**, 58 (1894).

[15] E. Knoevenagel and E. Speyer, *Chem. Ber.*, **35**, 395 (1902).

[16] W. Dieckmann and K. von Fischer, *ibid.*, **44**, 966 (1911).

[17] Substituent effects on aldol cyclization to unsaturated ketones are presently under investigation and will be discussed in a forthcoming publication. Both Michael and aldol cyclizations are favored by electron-releasing groups.

[18] A. T. Nielsen and W. J. Houlihan, *Org. Reactions*, in press: a review of the aldol condensation.



mono- and distyryl ketones **21** and **22**, respectively (**3** + **5** → **12**). Thus, the reaction could be extended, indirectly, to other methyl ketones, RCH_2COCH_3, with ArCHO. Within the known limits of synthesis of ketones **21** and **22**, limitations on substituents in Ar,[7,17] and the stated restrictions on Michael addition to form **23** and **24** (R′ = H), it should be possible to prepare several additional examples of diketone **24**. Also, mixed condensation products should be possible (products like **24**, R′ = H, having different R groups). For example, a product in which the ring-substituted R group = CH_3 and the side-chain R is hydrogen could arise by condensation of styryl ethyl ketone with dibenzalacetone.

Experimental Section[19]

1,5-Diphenyl-2-methyl-1,4-pentadien-3-one (5).—The procedure for preparation of dibenzalacetone from benzaldehyde and acetone[5] was extended to 2-butanone. To sodium hydroxide (100 g) in 1 l. each of water and ethanol was added, during 5 min, a mixture of benzaldehyde (106 g, one mole) and 2-butanone (36 g, 0.5 mole) keeping the temperature between 25–28°. The mixture was stirred vigorously at 25° for 21 hr, then extracted with methylene chloride. Removal of the solvents left 71.5 g of oil which on distillation gave, in addition to 10 g of forerun and a residue, 38.2 g of crude **5**, bp 180–195° (0.4 mm). Redistillation through a short column gave 8.0 g, bp 188° (0.3 mm), $n^{25}D$ 1.649. The elemental analysis and spectra indicate *ca.* 10–15% of an impurity (possibly pyrone **6**[6]) not removed by distillation: ν_{film} 1740 cm^{-1} (weak C=O), 1640 (conjugated C=O, strong); hydroxyl absorption absent; λ_{max}^{EtOH} 229 mμ (ε 12,300), 317 broad (19,000);[20] nmr (CCl_4) gave a sharp methyl singlet at τ 7.95 only and phenyl and vinyl bands centered at 2.4. Attempts to crystallize the material were unsuccessful;[21] it was used without further purification for the preparation of diketone **12** (see below).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 85.69; H, 6.83.

3,5-Diphenyl-2-methyl-4-propionylcyclohexan-1-one (7). A. From Styryl Ethyl Ketone (3).—Styryl ethyl ketone[3a] (3.2 g, 0.02 mole) was dissolved in 20 ml of absolute ethanolic sodium ethoxide (prepared from 50 mg of sodium). After standing at −15° for 38 months there was obtained 32 mg (1%) of crude diketone **7**, mp 176–177°. Recrystallization from ethanol gave 12.3 mg, mp 190–191°. The infrared and ultraviolet spectra were characteristic of those styryl alkyl ketone dimers obtained before:[7] ν_{KBr} C=O, doublet at 1725, 1700 cm^{-1}; OH absorption absent; λ_{max}^{EtOH} (ϵ_{max}) 243 (230), 248 (310), 253 (440), 258 (570), 265 (540), 268 (440), 287, broad (380); nmr ($CDCl_3$) showed characteristic ethyl multiplets; CH_2 quartet (τ 8.8) and CH_3 triplet (9.8), a methyl doublet (9.1), phenyl protons (10) at 2.7 and cyclohexane ring protons (6) broad multiplets 6.5–7.5. A solution of the substance ($8.76 \times 10^{-5} M$) in 80% ethanolic sodium hydroxide (0.5 *N*) revealed essentially no change in the absorption spectrum on standing at 25° for 67 hr.

B. From 3,5-Diphenyl-2-methyl-4-propionylcyclohexan-1-ol (14).—To a 0.32-g (0.001 mole) sample of ketol **14** (preparation described below) dissolved in 11 ml of acetic acid was added 1.1 ml of 0.67 *M* chromic acid solution (5.00 g of sodium dichromate dihydrate and 3.75 ml of 96% sulfuric acid diluted to 25 ml with water).[22] After shaking a few minutes the solution turned green and a solid separated. The mixture was diluted with water and filtered to yield 0.25 g (78%) of diketone **7**, mp 179–182°. Recrystallization from ethanol gave 0.17 g, mp 186–188°; further recrystallization gave small colorless prisms, mp 190–192°. When mixed with the sample of **7** obtained above from styryl ethyl ketone, the melting point was not depressed. Infrared and ultraviolet spectra of the two samples were identical.

Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55; mol wt, 320.41. Found: C, 82.63; H, 7.67; mol wt, 323.

4-(2-Benzalpropionyl)-3,5-diphenyl-2-methylcyclohexan-1-one (12). A. Condensation of Benzaldehyde with 2-Butanone.—To a solution of 318 g (3 moles) of benzaldehyde and 144 g (2 moles) of 2-butanone in 2 l. of absolute ethanol was added a solution of sodium ethoxide prepared from 10 g of sodium and 150 ml of absolute ethanol. The temperature was maintained at 25–30° by external cooling. After standing 5 days at room temperature the crystalline product was removed by filtration, 24.1 g (5.9%) of cream-colored prisms, mp 202–205°; most of the product crystallized from the reaction mixture within 2 days. Recrystallization from ethanol gave 21.0 g of white prisms, mp 205–207°; further recrystallization raised the melting point to 206.5–207.5°. When the reaction was conducted under similar conditions with a molar ratio of benzaldehyde to 2-butanone of 1:1 the yield of diketone **12** was 0.5%. With a ratio of benzaldehyde to 2-butanone of 3:1 under similar conditions a large quantity of sodium benzoate was produced (isolated as benzoic acid). Use of a higher molar ratio of sodium ethoxide or higher temperature failed to result in an increased yield of **12**.

B. Condensation of Styryl Ethyl Ketone (3) with 1,5-Diphenyl-2-methyl-1,4-pentadien-3-one (5).—A 4.96-g sample of 1,5-diphenyl-2-methyl-1,4-pentadien-3-one (**5**) (*ca.* 90% pure; see preparation above) and 3.20 g of styryl ethyl ketone (**3**)[3a,m] were added to ethanolic sodium ethoxide (prepared from 0.092 g of sodium and 50 ml absolute ethanol); the solution was allowed to stand at room temperature for 1 week. The colorless crystals of diketone **12** which separated were removed by filtration, 1.58 g (*ca.* 21%), mp 205–206°.

Anal. Calcd for $C_{29}H_{28}O_2$: C, 85.26; H, 6.91; mol wt, 408.51. Found: C, 85.15; H, 6.92; mol wt, 405.

Benzaldehyde (33 mg), 100 mg of 3,5-diphenyl-2-methyl-4-propionyl-1-cyclohexanone (**7**, described above) and 4 mg of sodium methoxide in 5 ml of absolute ethanol were heated on the steam bath for 3.5 hr. Unreacted **7** (8 mg, mp 184–192°) was recovered, but no diketone **12** or other crystalline product was isolated.

4-(2-Benzalpropionyl)-3,5-diphenyl-2-methylcyclohexan-1-ol (13).—A solution of diketone **12** (8.16 g. 0.02 mole) in 150 ml

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[19] Melting points were determined on a Kofler block and are corrected. Ultraviolet spectra were determined on a Cary Model 14 spectrophotometer, infrared spectra were determined on a Perkin-Elmer Model 137 spectrophotometer, and nmr spectra were determined on a Varian A-60 spectrometer (10–20% solutions in deuteriochloroform). Magnesium sulfate was employed as a drying agent.

[20] The bis-2-methoxy derivatives of **5**, $2\text{-}CH_3OC_6H_4CH{=}CHCOC(CH_3){=}CHC_6H_4\text{-}2\text{-}OCH_3$, yellow prisms, mp 94–96°, having spectra similar to that of **5**, has been prepared (4% yield) by a procedure similar to that described here (unpublished work, this laboratory). *Anal.* Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54; mol wt, 308.3. Found: C, 78.37; H, 6.68; mol wt, 308. Infrared and ultraviolet spectra gave ν_{KBr} 1645 cm^{-1} (C=O) and λ_{max}^{EtOH} 239 mμ (ε 14,900), 345 (20,800). Spectra of other distyryl ketones have been measured and discussed:[13a] $(C_6H_5CH{=}CH)_2C{=}O$, λ_{max}^{EtOH} 330 mμ (ε 34,600); $[(C_6H_5CH{=}C(CH_3)]_2C{=}O$, λ_{max}^{EtOH} 287 mμ (ε27,500).

[21] The actual preparation of **5** has been reported only once.[3f,g,i,s] Condensation of benzaldehyde with 2-butanone (refluxing aqueous hydrochloric acid) gave an oil, bp 224–226° (15 mm); elemental analyses were not given.[3i] After several crystallizations from ethanol a colorless crystalline solid, $C_{18}H_{16}O$ (mp 73°, yield not stated) described as **5**, was isolated from the oil.[3i] Our attempts to prepare *pure* **5** by condensation of benzaldehyde with 2-butanone or styryl ethyl ketone, with hydrogen chloride or hydrochloric acid catalyst, were unsuccessful; however, crude samples of **5** (based on spectral data) could be prepared.

[22] H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

of 95% ethanol and 0.3 g of platinum oxide catalyst were shaken in a Parr apparatus at 40–50 psi, 25°, until hydrogen uptake ceased (total of 1.0 mole equiv absorbed during 12 hr). The mixture was filtered and the filtrate was concentrated to dryness. The residue was crystallized from cyclohexane to yield 7.52 g (92%) of ketol **13**, mp 125–129°. Recrystallization from cyclohexane gave tiny needles: mp 126–127°; ν_{KBr} 3600 cm^{-1} (OH); 1650 (C=O conjugated); λ_{max}^{EtOH} 284 mμ (ϵ 13,900). The unconjugated carbonyl band (1720 cm^{-1}) present in the starting compound was absent.

Anal. Calcd for $C_{29}H_{30}O_2$: C, 84.84; H, 7.37. Found: C, 84.75; H, 7.46.

3,5-Diphenyl-2-methyl-4-propionylcyclohexan-1-ol (14).—A mixture of a 1.75-g sample of ketol **13**, 50 ml of water, 50 ml of 95% ethanol and 4 g of sodium hydroxide was heated in a stainless steel bomb at 25–190° for 3 hr, then at 190° for 19 hr. The mixture was concentrated to a small volume *in vacuo* and the product was filtered and washed with water to yield 1.34 g, mp 125–135°. Recrystallization from cyclohexane gave 0.75 g, mp 138–140°; further recrystallization gave small prisms, mp 140–141°, ν_{KBr} 3400 cm^{-1} (OH) and 1690 (C=O).

Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13; mol wt, 322.4. Found: C, 81.87; H, 8.21; mol wt, 318.

From the aqueous part benzaldehyde 2,4-dinitrophenylhydrazone was ultimately isolated, mp 237–238°; when mixed with an authentic sample (mp 238–239°) the melting point was 238–239°.

3,5-Diphenyl-2-methyl-4-propionylphenol (15).—A 1.5-g sample of ketol **14** and 0.3 g of 10% palladium on charcoal catalyst were mixed thoroughly in a test tube and the mixture was heated with a flame in a nitrogen atmosphere for 30 min, maintaining a temperature of 300–320° within the liquid. After cooling, the mixture was thoroughly extracted with hot chloroform and the extracts filtered and concentrated to yield 1.23 g of oil. Crystallization from benzene gave 30 mg of phenol **15**, mp 200–210°; recrystallization gave prisms, mp 220–221°, ν_{KBr} 3290 cm^{-1} (OH) and 1650 (conjugated C=O). The substance produced no color change in aqueous ethanolic ferric chloride solution. Attempts to prepare **15** by dehydrogenation of 3,5-diphenyl-2-methyl-4-propionylcyclohexan-1-one (**7**) under the above conditions led to recovered **7** as the only crystalline product; much oil (possibly mainly **3**) was formed.

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.39; H, 6.40.

6-Carbethoxy-3,5-diphenyl-2-cyclohexen-1-one (18).—Ethyl acetoacetate (52.0 g, 0.4 mole) and benzalacetophenone (83.3 g, 0.4 mole) were added to an ethanolic solution of sodium ethoxide (prepared by dissolving 1.0 g of sodium in 500 ml of absolute ethanol) and the solution was heated under reflux for 15 hr. Acetic acid (4.0 ml) was added to the hot solution and the clear yellow solution was chilled to 0° to deposit 96.1 g (75%) of keto ester **18**, mp 108–110°. Recrystallization from 95% ethanol gave 90.3 g of colorless prisms, mp 112–113° (lit.[15,16] mp 111–112°).

Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29. Found: C, 78.74; H, 6.16.

6-Carbethoxy-3,5-diphenyl-6-methyl-2-cyclohexen-1-one (19). 6-Carbethoxy-3,5-diphenyl-2-cyclohexen-1-one (**18**) (32.0 g, 0.1 mole) was dissolved in ethanolic sodium ethoxide solution (prepared by dissolving 2.3 g of sodium in 100 ml of absolute ethanol). To this solution was added 19 g (0.134 mole) of methyl iodide and the solution heated at 43° for 17 hr, and at 70–80° for 6 hr (solution neutral). The solution was cooled, 25 ml of water was added, and the mixture concentrated *in vacuo* to remove most of the ethanol. The residue was diluted with water and the product removed by filtration, 33.4 g (100%), mp 75–80°; recrystallization from dilute ethanol gave 30.9 g (92.5%) of large, colorless prisms of **19**, mp 84–87°.

Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.01; H, 6.63. Found: C, 78.93; H, 6.65.

3,5-Diphenyl-6-methyl-2-cyclohexen-1-one.—A mixture of 12.1 g of keto ester **19**, 100 ml of acetic acid, 20 ml of concentrated sulfuric acid, and 20 ml of water was heated under reflux until gas evolution ceased (5 days). The mixture was concentrated *in vacuo* to a volume of *ca.* 40 ml, chilled, and diluted with water. The oily product was crystallized from cyclohexane–hexane to yield 1.5 g, mp 68–70°; recrystallization gave prisms, mp 72–73°, ν_{Nujol} 1660 cm^{-1} (C=O, conjugated).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91. Found: C, 87.14; H, 6.94.

3,5-Diphenyl-2-methylphenol (17). A. From 6-Carbethoxy-3,5-diphenyl-6-methyl-2-cyclohexen-1-one (19).—A 2-g sample of keto ester **19** and 0.3 g of 10% palladium–charcoal were intimately mixed and heated with a flame (nitrogen atmosphere) in a test tube for 0.5 hr (temperature 320° in the liquid). The product was separated from the catalyst by several extractions with boiling chloroform; evaporation of the chloroform gave 1.5 g of oily product which was crystallized from cyclohexane–hexane to yield **17**, 0.80 g (51%), mp 94–96°, and 0.13 g, mp 89–91°.

B. From 3,5-Diphenyl-6-methyl-2-cyclohexen-1-one.—A 0.95-g sample of the ketone and 0.3 g of 10% palladium–charcoal were heated in the same manner as with **19**, above (15 min). Crystallization of the crude product (0.76 g) from cyclohexane gave 0.32 g, mp 94–97°, and 0.1 g, mp 75–90°.

C. From 4-(2-Benzalpropionyl)-3,5-diphenyl-2-methylcyclohexan-1-one (12).—A 2-g sample of diketone **12** and 0.3 g of 10% palladium–charcoal catalyst were heated as with **19**, above, for 15 min (325–355°). After cooling, camphorsulfonic acid (20 mg) was added and the mixture heated in an oil bath for 5.3 hr, the temperature being steadily raised from 160–205°. The product, and that from a second identical run, were combined and extracted with hot chloroform and filtered; the filtrate was concentrated to dryness. The residue (3.52 g) was treated with 20 g each of water, ethanol, and sodium hydroxide and the mixture was heated under reflux for 17 hr. The cooled mixture was diluted with water and extracted with ether; the dried extracts were evaporated to leave 2.66 g of red oil. Fractional crystallization of the oil from hexane gave 3,5-diphenyl-2-methylphenol (**17**), mp 95–97°. The aqueous alkaline portion was acidified to yield, ultimately, 0.2 g of oil from which no crystalline material could be isolated from benzene or cyclohexane solvent.

D. From 3,5-Diphenyl-2-methyl-4-propionylphenol (15).—A 15-mg sample of keto phenol **15** and 1 mg of camphor sulfonic acid were heated at 200–225° for 75 min. The black residue, which had a propionic acid odor, was treated with 2 g each of water, ethanol, and sodium hydroxide, The mixture was heated under reflux for 18 hr, then concentrated to near dryness. The residue was extracted with methylene chloride and the extracts were concentrated to dryness. Trituration of the residue gave crystals of 3,5-diphenyl-2-methylphenol (**17**), mp 92–95°; when mixed with an authentic sample, mp 93–96°, the melting point was 92–95°.

Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19; mol wt, 260.32. Found: C, 87.63; H, 6.30; mol wt, 259.

Registry No.—**5**, 14164-67-1; bis-2-methoxy derivative of **5**, 14164-68-2; **7**, 14164-69-3; **12**, 14271-40-0; **13**, 14164-70-6; **14**, 14164-71-7; **15**, 14164-72-8; **17**, 14164-73-9; **18**, 6287-66-7; **19**, 14164-75-1; 3,5-diphenyl-6-methyl-2-cyclohexen-1-one, 14164-76-2; benzaldehyde, 100-52-7; 2-butanone, 78-93-3.

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