the contention that a pore diffusional effect superimposed on an intrinsic zero-order dependence is responsible for the square-root hydrogen dependence which is observed. A zero-order dependence on hydrogen pressure is quite consistent with hydrogen/palladium ratios of ~0.6 near 1 atm at 25°.[23] The palladium crystallites at the exterior of the support, and those close to it, can be regarded to be reservoirs of hydrogen. It follows that a zero-order hydrogen dependence should be observed on palladium films but we do not have any evidence to this point.

Registry No.—Bicyclo[2.2.1]heptene, 498-66-8; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; cyclohexane, 110-82-7.

(23) F. A. Lewis, "The Palladium Hydrogen System," Academic Press, New York, N. Y., 1967, p 4.

Base-Catalyzed Intermolecular Condensation of α,β-Unsaturated Ketones. Self-Condensation of Styryl Isobutyl Ketone to Epimeric Diketones, $C_{26}H_{32}O_2$, and a Triketone, $C_{39}H_{48}O_3$. Stereochemistry of Michael Cyclization

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The self-condensation of styryl isobutyl ketone (**1**) in ethanolic sodium hydroxide solution leads to a cyclic diketone dimer, all-*trans*-3,5-diphenylisopropyl-4-(3-methylbutanoyl)cyclohexanone (**2a**), and a triketone trimer, 3,5-diphenyl-2-isopropyl-4-(2-isopropyl-7-methyl-5-oxo-3-phenyloctanoyl)cyclohexanone (**4**). In aqueous sodium hydroxide, **1** produces an acyclic dimer, 1,5-diphenyl-4-isopropyl-9-methyl-1-decene-3,7-dione (**3a**), a compound shown to be a precursor of **2a**. Pyrolysis of trimer **4** produces **1** and **2b**, an epimer of **2a**. Heating **2a** in refluxing dioxane with sodium methoxide catalyst leads to a mixture of **2a**, **2b**, and a third cyclic dimer, **2c**. The configurations of these condensation products have been established by deuterium-exchange experiments and nmr spectroscopy. The stereochemistry of the relevant addition reactions and a comparison with the related Michael aldol cyclization are examined and discussed.

Study of the stereochemistry of Michael cyclization arising from an acyclic precursor appears in only one previous report.[1] Stereochemistry of the related Michael aldol cyclization (Robinson annelation reaction) has been examined; most of these reactions involve Michael addition of a cycloalkanone enolate to an α,β-unsaturated ketone, followed by aldol cyclization to form a new ring.[2] Most other studies of Michael addition stereochemistry have dealt with the formation of acyclic diastereoisomers,[2f,g,3-5] or products of an addition to an activated endocyclic double bond.[2a,c,6-8] We have extended our studies of the base-catalyzed self-condensation of α,β-unsaturated ketones[9] to an examination of the stereochemistry of Michael cyclization products obtained by self-condensation of styryl isobutyl ketone. In this example, unlike many other types of Michael addition, the mechanism does not involve the complicating features of enolization stereochemistry. Product equilibration by enolization is a post-Michael addition process in this case.

The base-catalyzed self-condensation of styryl isobutyl ketone (**1**), in contrast to reactions of other

$$C_6H_5CH{=}CHCOCH_2C_3H_7\text{-}i$$
1

styryl alkyl ketones which have been examined,[9,10] leads to several crystalline condensation products rather than a single cyclic diketone dimer. Isomeric acyclic and cyclic diketones, $C_{26}H_{32}O_2$, and a triketone, $C_{39}H_{48}O_3$, have been prepared in the present work.

The base-catalyzed self-condensation of styryl isobutyl ketone has been studied by other workers.[9b,10c,11,12] In *ethanolic* sodium hydroxide solution the formation of a crystalline dimer, $C_{26}H_{32}O_2$, has been reported, and previously we showed its structure to be **2a**.[9b] We have now prepared dimers **2b** and **2c**, both of which have been shown to be epimers of **2a**. In *aqueous* sodium hydroxide Metayer[11] obtained a product, mp 141°, which he described as a dimer; we have shown it to be a trimer, $C_{39}H_{48}O_3$.

Condensation Products and Structure.—Self-condensation of styryl isobutyl ketone in *aqueous* sodium

(1) F. Wingler and H. Reiff, *Ann. Chem.*, **705**, 96 (1967).

(2) (a) W. S. Johnson, S. Shulman, K. L. Williamson, and R. Pappo, *J. Org. Chem.*, **27**, 2015 (1962); (b) J. A. Marshall and W. I. Fanta, *ibid.*, **29**, 2501 (1964); (c) H. G. O. Becker, U. Fratz, G. Klose, and K. Heller, *J. Prakt. Chem.*, (4) **29**, 142 (1965); (d) A. T. Nielsen, *J. Org. Chem.*, **30**, 3650 (1965); (e) T. A. Spencer, H. S. Neel, and D. C. Ward, *ibid.*, **31**, 434 (1966); (f) M. M. Robison, M. G. Pierson, L. Dorfman, and B. F. Lambert, *ibid.*, **31**, 3206, 3213 (1966); (g) L. Jung, *Bull. Soc. Chim. Fr.*, 4692, 4696 (1967); (h) A. T. Nielsen and W. J. Houlihan, *Org. Reactions*, **16**, 11 (1968).

(3) A. Wettstein, K. Heusler, H. Ueberwasser, and P. Wieland, *Helv. Chim. Acta*, **40**, 323 (1957).

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(7) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 367-368.

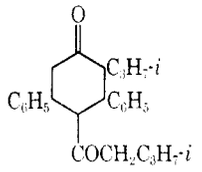
(8) (a) R. A. Abramovitch and J. M. Muchowski, *Can. J. Chem.*, **38**, 557 (1960); (b) S. V. Kessar, J. P. Nagpal, and K. K. Khullar, *J. Indian Chem. Soc.*, **39**, 381 (1962); (c) M. E. Wall, F. I. Carroll, and G. S. Abernathy, *J. Org. Chem.*, **29**, 604 (1964); (d) N. L. Allinger and C. K. Riew, *Tetrahedron Lett.*, 1269 (1966); (e) R. A. Abramovitch and D. L. Struble, *Tetrahedron*, **24**, 357 (1968).

(9) (a) A. T. Nielsen, D. W. Moore, and K. Highberg, *J. Org. Chem.*, **26**, 3691 (1961); (b) A. T. Nielsen and H. J. Dubin, *ibid.*, **28**, 2120 (1963); (c) A. T. Nielsen, H. Dubin, and K. Hise, *ibid.*, **32**, 3407 (1967); (d) A. T. Nielsen and S. Haseltine, *ibid.*, **33**, 3264 (1968).

(10) (a) R. Dickinson, I. M. Heilbron, and F. Irving, *J. Chem. Soc.*, 1888 (1927); (b) I. M. Heilbron and F. Irving, *ibid.*, 2323 (1928); (c) I. M. Heilbron and F. Irving, *ibid.*, 931 (1929); (d) I. M. Heilbron, R. N. Heslop, F. Irving, and J. S. Wilson, *ibid.*, 1336 (1931).

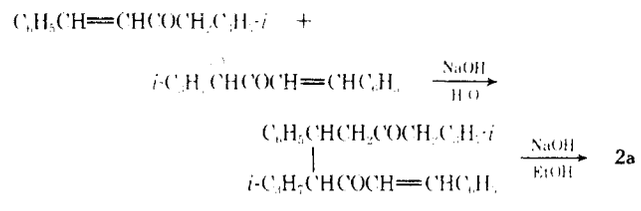
(11) M. Metayer, *Rec. Trav. Chim. Pays-Bas*, **71**, 153 (1952).

(12) C. V. Gheorghiu and B. Arwentiev, *J. Prakt. Chem.*, (2) **118**, 295 (1928).



2a, mp 207–208°
b, mp 170–172°
c, mp 94–96°

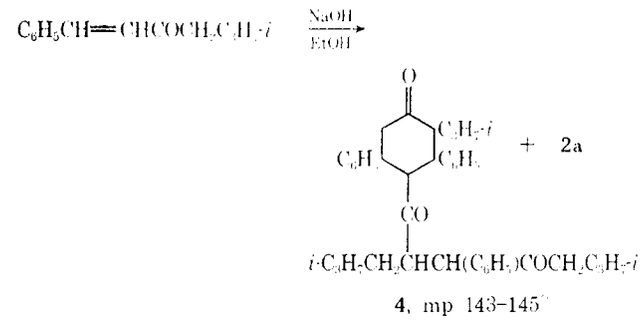
hydroxide at 50° (15–24 hr) gave as the principal product the acyclic Michael adduct **3a** (18–23% yield). The elemental analysis, molecular weight, spectra, and chemical behavior support structure **3a.** In ethanolic



3a, mp 115–117°

sodium hydroxide solution **3a** is converted essentially quantitatively into cyclic dimer **2a**; no other products result under a variety of conditions. Diketone **3a** is the first reported acyclic styryl alkyl ketone dimer.[13,14] Such acyclic dimers have been postulated as primary Michael adduct intermediates in the base-catalyzed self-condensation of styryl alkyl ketones.[9b–d]

Self-condensation of styryl isobutyl ketone in *ethanolic* sodium hydroxide gave, in addition to cyclic dimer **2a** (22–38% yield), a trimeric triketone, $C_{39}H_{48}O_3$, in 43–46% yield. Elemental analysis, molecular weight, spectra, and chemical behavior support structure



4, mp 143–145°

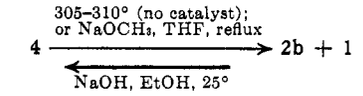
4. No evidence of olefinic unsaturation appears in the infrared and ultraviolet spectra.

Compound **4** appears to be the first trimer obtained by self-condensation of an α,β-unsaturated ketone. It also represents the first 3:3 aldehyde:ketone aldol condensation product to be described.[2h,9c]

(13) Acyclic, olefinic 1,5-diketones have been isolated as dimeric products of base-catalyzed self-condensation of a few other α,β-unsaturated ketones including (a) 4-methyl-1-phenyl-2-penten-1-one [R. Anet, *J. Org. Chem.*, **26**, 246 (1961)]; (b) 1-cyclopropyl-4-methyl-2-penten-1-one;[9a] and (c) 1,3-diphenyl-2-buten-1-one (dypnone) [H. Meerwein, *Chem. Ber.*, **53**, 1829 (1920)]. The dimers isolated in examples a and b were shown to be β,γ-unsaturated 1,5-diketones. Like **3a** they are derived from monomers containing isopropyl groups.

(14) The acyclic diketone dimer derived from mesityl oxide [*i.e.*, $(CH_3)_2C(CH_2COCH_3)CH_2COCH{=}C(CH_3)_2$] could not be isolated, but has been trapped as a bromo derivative: B. Furth and J. Wiemann, *Bull. Soc. Chim. Fr.*, 1819 (1965).

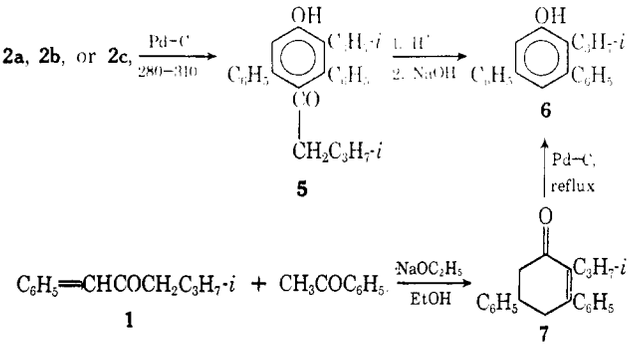
Heating trimer **4** at 305–310° for a few minutes resulted in retro-Michael cleavage in the side chain to yield only cyclic dimer **2b** and styryl isobutyl ketone **1**. The retrogression could also be effected by heating **4** under reflux in tetrahydrofuran with sodium methoxide catalyst. Trimer **4** was synthesized by base-catalyzed condensation of **1** with dimer **2b**.



A third cyclic dimer (**2c**) and dimer **2b** were obtained by heating dimer **2a** under reflux in dioxane with sodium methoxide catalyst. Nearly quantitative conversion of **2c** into **2b** occurred rather rapidly in ethanolic sodium hydroxide at 25°. This conversion could also be effected by heating **2c** in the absence of a catalyst at 300–310°.

The structures of cyclic dimers **2b** and **2c** were established by dehydrogenation, as with **2a**, by heating with palladium–charcoal to produce 3,5-diphenyl-2-isopropyl-4-(3-methylbutanoyl)phenol (**5**) (Scheme I), identical with a sample of this substance obtained from **2a**.[9b,15] Reverse Fries rearrangement, followed by saponification, led to phenol **6**, which was synthesized by dehydrogenation of 3,5-diphenyl-2-isopropyl-2-cyclohexen-1-one (**7**). The latter ketone was obtained in a Michael aldol cyclization departing from styryl isobutyl ketone (**1**) and acetophenone (Scheme I).

SCHEME I

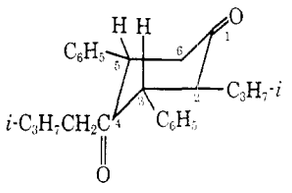


Stereochemistry.—Three stable diastereoisomers having cyclic dimer structure **2** are to be expected in basic medium (assuming a chair form of the cyclohexanone ring with favored equatorial substituents), since substituents at C-2 and C-4 may easily change configuration by equilibration. Exchange of all six enolizable hydrogens in **2a** and **2b** occurred within a few minutes in refluxing deuterioethanol–sodium ethoxide as shown by the nmr spectrum of the recovered deuterated product.

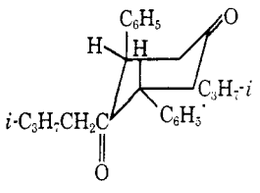
The two nonexchangeable C-3 and C-5 ring benzyl protons in hexadeuterio **2a** appear as a singlet at τ 6.67, and in hexadeuterio **2b** as two singlets at τ 6.30 and 6.18. These data suggest an all equatorially substituted structure for **2a**.

(15) The major product of dehydrogenation of **2b** is dimer **2a** (20% yield), believed to result by hydrogenation of certain products or intermediates formed by dehydrogenation of **2b**. Dimer **2a** was observed to have much greater thermal stability than **2b**. Dehydrogenation of dimer **2a** under the conditions employed with **2b** led to 31% recovery of **2a** and a 23% yield of phenol **5**.[9b] The relative low yield (5%) of **5** from **2b**, produced without recovery of **2b**, is believed to be due to the low thermal stability of **2b** under the reaction conditions. The thermal stability of the cyclic dimers decreases in the order **2a** > **2b** > **2c**.

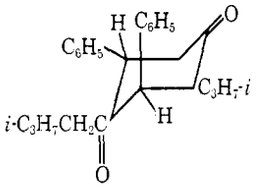
Additional evidence for structure **2a** is shown by the nmr spectra in Table I. In **2a** the C-4 substituents are symmetrically disposed with respect to the C-3 and C-5 phenyl substituents; the signal of the strongly



2a



2b



2c

shielded magnetically equivalent isopropyl methyl protons of the C-4 3-methylbutanoyl group appears as a 6.5-Hz doublet centered at τ 9.78. By contrast, in **2b** the C-4 isopropyl methyl signal appears as a pair of magnetically nonequivalent,[16] less shielded 6.5-Hz doublets centered at τ 9.47 and 9.59; in **2c** these doublets appear at τ 9.23 and 9.32. The isobutyl methylene doublet is also strongly shielded in **2a** (τ 8.83), but less so in **2b** (τ 8.33). In acyclic dimer **3a** this doublet appears at τ 7.88, and in styryl isobutyl ketone at τ 7.52.

TABLE I

NMR PEAKS OF ISOPROPYL METHYL GROUPS[a] AND STEREOCHEMISTRY OF STYRYL ISOBUTYL KETONE CONDENSATION PRODUCTS

	i-C_3H_7 at C-2[b]		*i*-C_3H_7CHCO- at C-4[b]		*i*-$C_3H_7CH_2$,	C_6H_5 confign at
Compd	τ	$\Delta\tau$	τ	$\Delta\tau$	acyclic, τ	C-3, C-5[d]
2a	8.96, 9.11	0.15	9.78, 9.78[c]	0.00[c]		e, e
2b	8.92, 9.11	0.19	9.47, 9.59	0.12		e, a
2c	8.98, 9.37	0.39	9.23, 9.32	0.09		a, e
4	8.97, 9.03	0.06	9.47, 9.63	0.16	9.22[c]	e, a
3a	8.89, 9.01	0.12			9.23[c]	
1					9.03[c]	

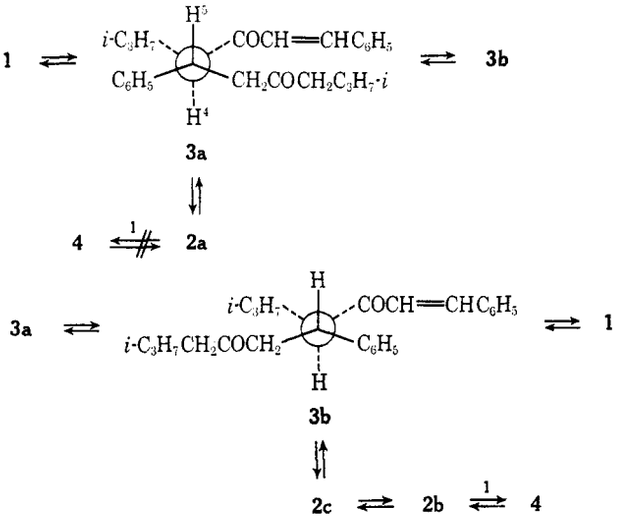
[a] Center of doublet ($J \cong$ 6.5–7.0 Hz), measurement in deuteriochloroform with tetramethylsilane internal reference. [b] C-2 and C-4 positions of cyclohexanone ring except in **3a**. [c] Isopropyl methyl signals magnetically equivalent within limits of resolution. [d] e = equatorial; a = axial.

Available evidence suggests that in **2b** the C-5 phenyl is axial with the remaining substituents equatorial; in **2c** only the C-3 phenyl is axial. Isomer **2b** is thermodynamically more stable than **2c**, as was pointed out above. Comparison of the C-2 isopropyl methyl signals in the three isomers (Table I) reveals nearly identical chemical shifts for the 6.5-Hz methyl doublet pair in **2a** and **2b**, but different chemical shifts in **2c**. Also, it is noted that the methyl chemical shift differences due to magnetic nonequivalence in **2a** and **2b** are similar ($\Delta\tau$ = 0.15 and 0.19, respectively) and much less than the value found for **2c** ($\Delta\tau$ = 0.39). Together, these values suggest an identical configuration of C-2 isopropyl and C-3 phenyl in **2a** and **2b**, which is different from the configuration of these groups in **2c**.

Other cyclic styryl alkyl ketone dimers[9,10] are believed to have an all-*trans*-equatorial configuration like that of **2a**.

Two acyclic styryl isobutyl ketone dimers are possible. Only one of these could be isolated in the present work. It is believed to have configuration **3a** (Scheme II), a conclusion based principally on chemical evidence which also disfavors configuration **3b**. A preferred conformation with *trans* disposition of C-4, C-5 hydrogens is in agreement with the nmr spectrum.

SCHEME II



Acyclic dimer **3a** produces cyclic dimer **2a** under a wide variety of reaction conditions; yields are often quantitative and other products are not produced. In particular, under the usual reaction conditions (ethanolic sodium hydroxide, 25°), whereby styryl isobutyl ketone (**1**) produces trimer **4**, no products other than **2a** are produced from **3a** *even in the presence of a large excess of* **1**. In another experiment, 50% **3a**, and no other product, was recovered from a reaction in which **2a** is formed in 30% yield, suggesting that the equilibration **3b** ⇄ **3a** does not occur under these conditions. Preparation of **2a** from **3a** in deuterioethanol–sodium ethoxide led only to hexadeuterio **2a**.

Acyclic dimer **3b** could not be isolated. It is believed that its isolation is disfavored under all reaction conditions, and that it undergoes very rapid cyclization to **2c**, followed by rapid conversions of **2c** to **2b** and **4**.

The conversion **3a** → **2a** appears to be a product-development-controlled process.[17] Stereochemistry of enolization is not involved in this apparently kinetically controlled Michael cyclization; anion protonation at C-6 represents the final Michael step (nonstereochemically important), and subsequent enolization at C-2 or C-4 can result in equilibration only as a post-

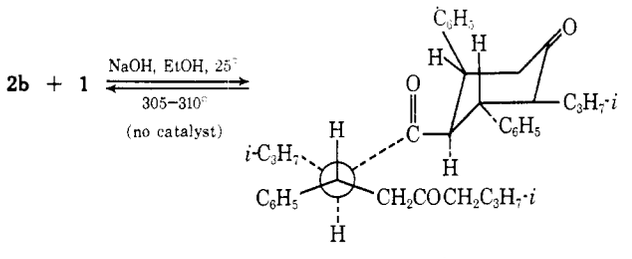
(16) (a) M. Kajtár and L. Radics, *Chem. Commun.*, 784 (1967); (b) T. S. Sorensen, *Can. J. Chem.*, **45**, 1585 (1967).

(17) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966).

Michael addition event. Dimer **2a** is formed under reaction conditions which do not permit its retrogression to **3a**, nor equilibration of **3a** to **3b**. Furthermore, the epimerization **2b** → **2a** is disallowed. The cyclization of **3a** could lead to a maximum of four diastereoisomers, *two of which could equilibrate at C-2 and C-4 to produce* **2b** under the reaction conditions. No **2b** is formed. It is suggested that in the transition state leading to the most stable product, **2a**, there is a *trans* disposition of all bulky groups, at or removed from the bond-forming site. This situation is also found in a Michael aldol cyclization involving formation of a six-membered ring having four asymmetric centers, although a very small amount (*ca.* 5%) of a less stable product (COH epimer) is formed under conditions of kinetic control.[2d] This result agrees with an earlier suggestion that more stereoselectivity is to be expected in the Michael addition, relative to the aldol condensation.[2d]

Conversion of cyclic dimer **2a** to dimers **2b** and **2c** in refluxing dioxane–sodium methoxide requires a retrogression of **2a** to acyclic dimer **3a** (Scheme II), and very likely an equilibration **3a** ⇄ **3b** as well. A higher temperature and an aprotic solvent permit a less stable isomer (**2c**) in the equilibrium.[4,5] Chilling, followed by neutralization of the catalyst, leads to isolation of **2c**. Assuming a *trans* orientation of C-4 and C-5 groups resulting by Michael cyclization of **3b**, in the manner envisioned for **3a**, the initial cyclization product from **3b** should be **2c**, which can then readily equilibrate to **2b** by enolization at C-2 and C-4.

The configuration of trimer **4** is suggested by its synthesis from cyclic dimer **2b** and styryl isobutyl ketone, and the formation of these components and no others (no **2a**) by heating **4** at 310°. Although **4** can also arise



4

from **2c**, **4** is believed to have the same configuration of substituents in the cyclohexane ring as does **2b**, since **2b** has been shown to be thermodynamically much more stable, relative to **2c**, in ethanolic sodium hydroxide.

The nmr spectrum of **4** supports the assigned stereochemistry (Table I). In **4** the values for the chemical shifts of the C-2 isopropyl methyls (τ 8.97, 9.03) and the chemical shift difference of these methyls due to magnetic nonequivalence ($\Delta\tau$ = 0.06) are smaller and resemble more closely the corresponding values for **2a** and **2b** than the values for **2c**. Also, these values for the signals of the methyls of the 3-methylbutanoyl group attached at C-4 are nearly identical in **2b** and **4**, but different from the values for **2a** and **2c**. These facts suggest an identical configuration of C-2 isopropyl and C-3 phenyl in **2a**, **2b**, and **4**, which is different from that in **2c**, as well as an identical configuration of C-4 substituent and C-5 phenyl in **2b** and **4** which is different from the configuration of these groups in **2a** and **2c**.

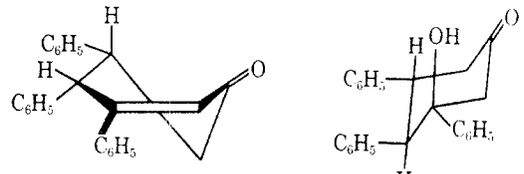
The C-4 side-chain configuration in **4** may exist as illustrated by the Newman projection. The nmr spectra of **4** and acyclic dimer **3a** are very similar with respect to the peaks in the spectrum of those substituents located in the region of the acyclic diastereoisomerism. An isobutyl methyl doublet appears at τ 9.22 (9.23) and a sharp phenyl signal at τ 2.63 in both compounds. The peaks of the single acyclic protons in **4** (shown in a favored *trans* conformation as with **3a**) could not be sufficiently resolved to make assignments.

The reaction sequence which leads to trimer **4** is not necessarily established by synthesis of **4** from dimer **2b** and styryl isobutyl ketone (**1**). However, the available data suggest no reasonable precursors other than **2b**, **2c**, and **1**. Dimers **2a**, **3a**, and **3b** appear to be excluded. The failure of **2a** to react with **1** to form any trimer may be attributed to a steric factor which reduces the reactivity, or inhibits the formation, of the required enolate anion of **2a**. Cyclization of **3a** to **2a** evidently occurs more rapidly than other condensation reactions which **3a** might undergo under the reaction conditions. Failure of **3a** to form a trimer by reaction with **1** suggests the likelihood that acyclic dimer **3b** is also not a precursor of trimer **4**. Acyclic dimer **3b** appears to cyclize even more rapidly than **3a**, since **3a** could be isolated as a reaction product in aqueous medium where no **2a** is formed, but where **4** and no **3b** form. Also, the higher yield of **4** relative to **2a** from **1** in ethanolic sodium hydroxide could be explained by assuming a more rapid cyclization of **3b** to **2c** relative to the **3a** → **2a** cyclization. Finally, formation of **4** from **3a** or **3b** requires that the three required, successive Michael additions occur in a sequence different from that whereby **4** is formed from **2b** or **2c**. The sequence from **3a** or **3b** would make it difficult to explain the observed stereochemistry of **4**, since by this route one might expect a trimer in which all cyclohexane substituents are equatorial.

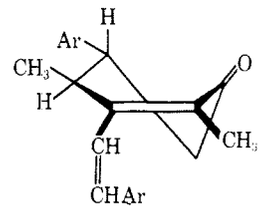
Formation of trimer **4** is unique. Other styryl alkyl ketones have not been observed to form trimers.[9,10] It is believed that the required enolate anion derived from **2b** or **2c** is a potent nucleophile, perhaps owing to its poor solvation, and is not too hindered to prevent Michael addition to a molecule of monomer. (It should be possible to prepare a mixed trimer from **2b** and a different monomer.) High crystallinity, low solubility, high melting point, and slow rate of retrogression to reactants may facilitate isolation of trimer **4**.

Michael stereochemistry results of the present investigation agree with those reports on Michael aldol cyclization departing from acyclic precursors obtained by Michael additions.[1,2d,f,5,9d] The monocyclic products formed in each of these base-catalyzed reactions (which include examples of kinetic and thermodynamic control) have *trans* stereochemistry in the carbon–carbon bond initially derived by Michael addition.

Compound **8** (thermodynamically favored[5]) is an exception (C-4, C-5 *cis*). The related cyclization products **9** (kinetically favored and formed from the same reactants as **8**[5]), and **10**[9d] both have C-4, C-5 *trans* stereochemistry. However, the exception may



9



10, Ar = 2-$CH_3OC_6H_4$

be explained by recognizing that in cyclohexene compounds (existing in a favored chair conformation[18-20]) eclipsing by a C-1 phenyl substituent on the double bond results in a favored pseudoaxial configuration of C-6 phenyl, and certain other C-6 substituents, particularly in a molecule lacking C-4 substituents.[5,20,21]

Experimental Section[22]

3,5-Diphenyl-2-isopropyl-4-(3-methylbutanoyl)cyclohexanone (Isomer 2a) and 3,5-Diphenyl-2-isopropyl-4-(2-isopropyl-7-methyl-5-oxo-3-phenyloctanoyl)cyclohexanone (4). Procedure A. Condensation of Benzaldehyde with Methyl Isobutyl Ketone.—To benzaldehyde (106 g, 1.0 mol) and methyl isobutyl ketone (100 g, 1.0 mol) dissolved in 680 ml of absolute ethanol was added 60 ml of 25% aqueous sodium hydroxide solution. The reaction flask was swept with nitrogen and sealed with a ground-glass stopper. The temperature rose spontaneously to a maximum of 39° within 5 min and the solution became orange-red. The solution was stored in the dark at room temperature. Crystals appeared in the solution within 15 hr and continued to separate for *ca.* 4 days, after which time very little further crystallization was observed. After a total reaction time of 1 week the mixture was filtered to yield 105.6 g of white crystals, mp 135–180°; concentration and chilling of the filtrate yielded 21.7 g, mp 130–140°. Crystallization of the first crop from ethyl acetate (900 ml) gave 32.5 g of **2a**, mp 207–208°, in addition to 9.5 g, mp 180–204°, obtained by concentration of the filtrate: total yield, 42 g, 22.3%; λ_{max} 248 mμ (ε 182), 253 (260), 259 (374), 266 (316), 268 (192), 295 (96); analytical data are in Table II.

Concentration of the ethyl acetate filtrate to dryness gave 60.0 g, mp 130–140°, which was combined with the crude second crop above (total yield of crude **4**, 81.7 g, 43.5%). Crystallization from ethanol gave 63.5 g of chunky prisms, mp 141–143°. Recrystallization gave 42.8 g: mp 143–145°; λ_{max} 248 mμ (ε 303), 253 (438), 259 (638), 265 (560), 268 (390), 299 (207); analytical data are in Table II.

Concentration of the filtrates remaining from the above crystallization gave 49.1 g of dark-red, viscous oil which was distilled to yield 1.33 g of crude benzyl alcohol, bp 68–71° (1.0 mm), and 12.7 g (6.8%) of styryl isobutyl ketone, bp 105–106° (0.4 mm). The viscous brown residue (34.2 g) crystallized from 100 ml of 95% ethanol deposited 0.17 g of crude dimer **2a**, mp 180–195°, and no other crystalline product.

The aqueous alkaline part remaining from the reaction work-up was acidified with hydrochloric acid to yield 2.77 g of material, mp 115–120°; recrystallization gave benzoic acid, mp 121–122°.

Procedure B. Self-Condensation of Styryl Isobutyl Ketone.—To styryl isobutyl ketone[11] (10.0 g, 0.053 mol) in 50 ml of absolute ethanol was added 1.6 ml of 25% aqueous sodium hydroxide solution. After standing 12 days at 25° in a nitrogen atmosphere there was obtained 4.70 g of crystals, mp 135–195°; from the filtrate by concentration and chilling there was obtained 1.92 g of **2a**, mp 205–206°, and 1.76 g of crude trimer **4**, mp 128–130°. Recrystallization of the first crop gave 1.87 g of **2a**, mp 204–206° (total yield of **2a**, 3.79 g, 38%). The remainder was crude trimer (total yield 4.59 g 46%).

1,5-Diphenyl-4-isopropyl-9-methyl-1-decene-3,7-dione (3a).—A mixture of styryl isobutyl ketone[11] (10 g, 0.053 mol), sodium hydroxide (1.0 g) and 2 ml of water was stirred at 50° for 15 hr. The mixture was cooled and extracted with ether. The extracts were washed with water and dried; the solvents were evaporated to leave 9.16 g of yellow oil. Crystallization from ethanol gave 1.57 g of diketone **3a**, mp 90–105°. From the filtrate by distillation there was obtained 6.78 g (67.8%) of recovered styryl isobutyl ketone, bp 105–110° (0.3 mm), and 0.97 g of residue. Crystallization of the residue from ethanol gave 0.2 g of crude trimer **4**, mp 120–130° (recrystallization from ethanol gave 0.15 g, mp 138–140°), and 0.20 g of additional diketone **3a**, mp 90–110°; total yield of **3a** 1.77 g (17.7%). Recrystallization from ethanol gave 0.8 g, mp 113–115°. Further recrystallization gave small needles: mp 115–117°; analytical data are in Table II; λ_{max}^{EtOH} 288 mμ (ε 21,000) [styryl isobutyl ketone λ_{max}^{EtOH} 289 mμ (ε 19,400)]. The nmr spectrum of **3a** shows two 16-Hz vinyl doublets (two *trans*-olefinic protons) centered at τ 2.71 and 3.62, a 6.5-Hz isobutyl methyl doublet centered at τ 9.23, and a pair of 6.5-Hz methyl doublets centered at τ 8.89 and 9.01; the two phenyl signals are observed at τ 2.63 and 2.80. The C-4 proton (H-4) signal appears at τ 6.95 (dd, $J_{4,5}$ = 8, J = 6 Hz), the C-5 proton (H-5) at τ 6.28 (eight-line multiplet, J = 6, 8, 9 Hz), and the two C-6 methylene protons as overlapping doublets centered at τ 7.16 (J = 6 Hz) and 7.18 (J = 8 Hz).

In a parallel 50-g run employing a reaction time of 24 hr there was obtained a 23% yield of diketone **3a**, 2% of trimer **4**, 2% of cyclic dimer **2b**, 1% of cyclic dimer **2a**, and 32% of recovered styryl isobutyl ketone. Treatment of the noncrystalline reaction product remaining (after removal of products **1**, **2a**, **3a**, and **4**) with ethanolic sodium hydroxide failed to yield any additional crystalline product. The shorter reaction time of the first run provides **3a** in slightly lower yield, but the material isolated is much more easily purified.

Cyclization of 1,5-Diphenyl-4-isopropyl-9-methyl-1-decene-3,7-dione (3a) to Cyclic Dimer 2a.—A 94.7-mg sample of acyclic diketone **3a** and 15 mg of sodium methoxide in 5 ml of absolute ethanol was heated at 70° for 7.5 hr. The cooled solution deposited 72.3 mg of cyclic diketone **2a**, mp 202–203°. The filtrate was neutralized with acetic acid, and chilled to −15° to deposit 19 mg of **2a**, mp 203–204°. Concentration of the filtrate to dryness and dilution with water gave 2.4 mg, mp 195–200°, and 1.0 mg, mp 165–195°; total yield of **2a**, 94.7 mg (100%).

Acyclic diketone **3a** (100 mg), 0.5 ml of 1 *N* sodium hydroxide (aqueous), and 5 ml of 95% ethanol heated at reflux for 1 min gave 30 mg of **2a**, mp 186–197°, and 50 mg of recovered **3a**, mp 87–97°. A parallel experiment employing a 5-min reflux time gave a 67% yield of **2a**, mp 199–205°.

Acyclic diketone **3a** (100 mg), 10 ml of ether, and 1 ml of 0.1 *N* aqueous sodium hydroxide solution were stirred at 25° for 4–6 hr; there resulted only unreacted **3a** which was crystallized from ethanol to yield 78–87 mg, mp 108–112°. Ketone **3a** (100 mg), sodium hydroxide (100 mg), water (2 ml), and benzene (10 ml) were stirred at 50–60° for 4 hr; there resulted 87 mg of unreacted **3a**, mp 102–103°.

Preparation of 3,5-Diphenyl-2-isopropyl-4-(3-methylbutanoyl)-cyclohexanone Isomers 2b and 2c from 2a.—A 20.0-g sample of cyclic dimer **2a** in 200 ml of dioxane containing 0.26 g of sodium methoxide was heated under reflux for 69 hr. After cooling the solution, neutralization of the catalyst with acetic acid, and removal of the solvent, the residue was crystallized from ethanol to yield 7.74 g, mp 195–198°, and 1.10 g, mp 170–185°, of recovered **2a** (44% total). By concentration and chilling of the filtrate there was obtained 1.74 g of crude dimer **2b**, mp 150–165°, 3.83 g of crude dimer **2b**–**c** mixture, mp 90–115°, and 5.24 g of viscous, noncrystalline material. Several recrystallizations of the crude dimer **2b** from ethanol gave 0.36 g, mp 165–170°. Further recrystallization gave 0.17 g of **2b**: mp 168–170°; an

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(22) Melting points were determined on a Kofler block and are corrected. Ultraviolet spectra were determined on a Cary Model 11 spectrophotometer (95% ethanol solvent), infrared spectra on a Perkin-Elmer Model 137 spectrophotometer, and nmr spectra on a Varian A-60 spectrometer (10–20% solutions in deuteriochloroform unless otherwise stated). Mass spectra were determined on a Hitachi Model RMU-6E. Magnesium sulfate was employed as a drying agent. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

TABLE II

PROPERTIES OF STYRYL ISOBUTYL KETONE CONDENSATION PRODUCTS

Compd	Bp (mm) or mp, °C	Infrared bands (KBr), cm⁻¹		Elemental analyses[a]		
		C=O	CH out-of-plane	% C	% H	Mol wt[b]
2a	207–208[c]	1720, 1690	700 s, 755 m, 767 w	83.07	8.53	376[d], 363[e]
2b	170–172[f]	1700	700 s, 737 m, 763 w, 780 m	82.96	8.88	376[d]
2c	94–96	1710, 1690	700 s, 757 m, 776 w	82.64	8.70	376[d]
3a	115–117	1710, 1640	700 s, 756 m	83.34	8.61	380[e]
4	143–145[g]	1710, 1680	703 s, 712 (sh) m, 752 w, 763 m	83.08	8.72	564,[d] 563[e]
1	105–106 (0.4 mm)[h]	1680, 1640[i]	690 s, 749 s[i]			

[a] Calcd for $C_{26}H_{32}O_2$ and $C_{39}H_{48}O_3$.: C, 82.93; H, 8.57. [b] Calcd for $C_{26}H_{32}O_2$: mol wt, 376.52. Calcd for $C_{39}H_{48}O_3$: mol wt, 564.77. [c] Lit. mp 202°,[10c] 205–206°,[9b] 209°.[11] [d] Determination by mass spectroscopy. [e] Determination by vapor osmometry. [f] Lit.[11] mp 170–171°. [g] Lit.[11] mp 141°. [h] Lit.[11] bp 159–160° (17 mm). [i] Measurement on neat liquid.

analytical sample had mp 170–172°; λ_{max} 248 mμ (ε 248), 253 (308), 259 (368), 266 (301), 268 (203), 295 (98); analytical data are in Table II.

Recrystallization of the crude dimer **2b–c** mixture from ethanol gave 2.0 g, mp 115–118°. Further recrystallization gave prisms of a 1:1 **2b–c** compound, mp 118–121°; recrystallization from hexane did not change the melting point. The mixture, which could not be separated by crystallization, was resolved by chromatography on silica gel (elution with benzene) to give equal weights of dimer **2b**, mp 170–172°, after recrystallization from ethanol, and **2c**, mp 94–96°, after recrystallization from heptane; analytical data are in Table II; the ultraviolet spectrum of **2c** is practically identical with that of **2a** and **2b**.

The infrared spectra of isomeric dimers **2a**, **b**, and **c** were virtually identical except for the 735–780-cm⁻¹ CH out-of-plane deformation region (KBr); *cf.* Table II. Differences in the nmr spectra of these isomers are discussed in the text.

Preparation of 3,5-Diphenyl-2-isopropyl-4-(3-methylbutanoyl)-cyclohexanone Isomer 2b. A. By Thermal Cleavage of Trimer 4.—A 6.0-g sample of trimer **4** was heated in a test tube with a flame at 305–310° for 12 min and at 320° for 1 min (thermometer bulb in liquid). After cooling the sample in a stream of nitrogen and crystallization of the residue from ethanol (25 ml) there was obtained 1.84 g (46%) of dimer **2b**, mp 163–166°. Recrystallization gave 0.85 g of long needles, mp 167–170°. Further recrystallization raised the melting point to 169–170°. Chilling of the filtrate gave 1.24 g (21%) of recovered trimer **4**, mp 130–145°. Concentration of the filtrate to dryness gave 2.77 g of oil which was distilled to yield 1.13 g (56%) of styryl isobutyl ketone, bp 108–110° (0.5 mm), and 1.66 g of residue. The styryl isobutyl ketone was identified by infrared spectra comparison with an authentic sample and its semicarbazone derivative, mp 170–172° [melting point undepressed when mixed with an authentic sample, mp 170–172° (lit.[23] mp 167°)].

B. By Base-Catalyzed Cleavage of Trimer 4.—A solution of 1.0 g of trimer **4** and 27 mg of sodium methoxide in 10 ml of tetrahydrofuran was heated under reflux for 21 hr. The solution was neutralized by addition of acetic acid and concentrated to dryness. Crystallization of the residue from ethanol gave 0.85 g of recovered **4**, mp 140–142°, and 21 mg of dimer **2b**, mp 165–168°. A similar experiment in refluxing absolute ethanolic sodium ethoxide gave 17% recovery of crude **4** and gummy material, but no other crystalline product.

C. By Thermal Epimerization of Cyclic Dimer 2c.—A 55.7-mg sample of dimer **2c** was heated in a small test tube at 300–310° for 2 min. Crystallization from ethanol gave 5.5 mg of dimer **2b**, mp 165–168°. Addition of 0.1 ml of 10% aqueous sodium hydroxide to the filtrate, followed by standing at room temperature for 3 hr, led to formation of an additional 15.0 mg of dimer **2b**, mp 169–170°.

D. By Base-Catalyzed Epimerization of Cyclic Dimer 2c.—A 3.9-mg sample of dimer **2c** in 0.5 ml of ethanol containing a few drops of 10% aqueous sodium hydroxide was allowed to stand at room temperature. Within *ca.* 1 hr crystals of isomer **2b** began to separate. After 16 hr the mixture was chilled to −15° for 2 hr, and then filtered to yield 3.3 mg of dimer **2b**, mp 167–169°.

Samples of dimer **2b** prepared by the above five methods all showed identical infrared spectra. Pairs of the samples prepared by the different methods, when mixed, each showed no depression in melting point.

A 100-mg sample of **2b** in 10 ml of ethanol containing 0.1 ml of 10% aqueous sodium hydroxide solution was allowed to stand at room temperature for 9 days; there resulted 39 mg of recovered **2b**, mp 160–165°, and no other crystalline product.

Pyrolysis of Styryl Isobutyl Ketone Dimers. A. Cyclic Dimers 2a, b, and c.—A 1.0-g sample of cyclic dimer **2a** heated under reflux (*ca.* 315–320° in the liquid) for 5 min followed by crystallization from ethanol led to recovered **2a**, 0.55 g, mp 201–203°, and 0.05 g, mp 191–197°. No other crystalline product could be isolated from the filtrate.

Similarly, a 0.50-g sample of cyclic dimer **2b** heated at 300 ± 5° for 5 min gave 0.37 g of recovered **2b**, mp 166–167°, after crystallization from ethanol, and no other crystalline product. Treatment of the filtrate with 20 mg of sodium methoxide, followed by heating on the steam bath for 5 min, led only to isolation of 0.03 g of additional **2b**, mp 165–170°. Thermal epimerization of cyclic dimer **2c** into isomer **2b** is described above.

B. Acyclic Dimer 3a.—A 0.50-g sample of acyclic dimer **3a** was heated under reflux for 4 min; during the heating the temperature within the liquid dropped from 320 to 305°. Cooling gave an oil which was dissolved in 10 ml of absolute ethanol containing 80 mg of sodium methoxide. Heating the resulting solution on the steam bath for 5 min, followed by chilling, led to isolation of 0.07 g of cyclic dimer **2a**, mp 200–205°.

Synthesis of Trimer 4.—A 55-mg sample of cyclic dimer **2b** and 275 mg of styryl isobutyl ketone (10 mol equiv) were dissolved in 4 ml of ethanol containing 0.1 ml of 10% aqueous sodium hydroxide; the solution was allowed to stand at room temperature for 16 hr. The resulting clear yellow solution was acidified with acetic acid and concentrated to a small volume. Chilling at −15° gave 32.9 mg (40%) of crude trimer **4**, mp 125–140°, and no other crystalline product. Recrystallization of the crude product from ethanol gave trimer **4**, mp 140–141°, identified by its infrared spectrum. When mixed with a sample of **4** obtained by the self-condensation of styryl isobutyl ketone, the melting point was not depressed.

A parallel experiment employing acyclic dimer **3a** failed to yield trimer **4**. A 188-mg sample of acyclic dimer **3a** and 1.88 g of styryl isobutyl ketone (20 mol equiv) were dissolved in 5 ml of ethanol containing 0.5 ml of aqueous sodium hydroxide solution; the solution was allowed to stand at room temperature for 15 hr. Crystals of cyclic dimer **2a** separated, 185 mg, mp 205–206°. Chilling the filtrate at −15° for 2 days led to 45 mg of additional **2a**, mp 195–205°.

Preparation of 1,3,6,6-Tetradeuterio-3,5-diphenyl-2-isopropyl-4-(2,2-dideuterio-3-methylbutanoyl)cyclohexanone Isomers (Hexadeuterio 2a and b).—A solution of 100 mg of cyclic dimer **2a** in 10 ml of ethanol-O-*d* containing sodium ethoxide (prepared by addition of 70 mg of sodium to the alcohol) was heated under reflux for 3 hr. Concentration to near dryness, followed by dilution of the residue with water, gave 80 mg of hexadeuterio **2a**, mp 200–202°. A 10-min reflux period led to a similar result. [A 1-hr reflux period with ethanolic sodium bicarbonate led only to exchange of the C-6 ring methylene protons as evidenced by a marked reduction in intensity of the nmr signal of these protons (multiplet at τ 7.3).] The nmr spectrum of hexadeuterio **2a** showed only the ten phenyl protons as a sharp singlet (τ 2.72), the two ring benzyl protons as a sharp singlet at τ 6.67, and the two isopropyl methine protons as a complex multiplet centered at τ 8.48; the remainder of the spectrum is discussed in the text. Signals observed in **2a** for the exchangeable enolizable protons at C-2, C-4, and C-6 in the cyclohexanone ring, and in the isobutyl methylene group, were absent in hexadeuterio **2a**.

In a similar experiment, 200 mg of cyclic dimer **2b** in 10 ml of

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deuterioethanol containing sodium ethoxide, prepared by addition of 10 mg of sodium to the alcohol, was heated under reflux for 7 min. Distillation of the solvent (in about 5 min) to reduce the volume to 5 ml, followed by chilling at −15°, led to 100 mg of hexadeuterio **2b**, mp 165–169°. Dimer **2b** was found to be much less stable than isomer **2a** in refluxing ethanolic sodium ethoxide. Heating under the above conditions for periods longer than 30 min resulted in destruction of dimer **2b**. However, complete deuterium exchange of all enolizable hydrogens occurred very rapidly within 5–10 min with isomers **2a** and **2b** under the conditions described. The nmr spectrum of hexadeuterio **2b** was different from that of hexadeuterio **2a**. The phenyl protons appeared as a τ 2.3–2.9 multiplet with a principal signal at τ 2.53, the two ring benzyl protons as singlets at τ 6.18 and 6.30, and the two isopropyl methine protons as a multiplet centered at *ca.* τ 8.3; the remainder of the spectrum is discussed in the text. As with hexadeuterio **2a**, proton signals of all six enolizable protons were absent in the spectrum of hexadeuterio **2b**.

Attempts to prepare deuterio derivatives of cyclic dimer **2c** and acyclic dimer **3a** were unsuccessful. Cyclic dimer **2c** rapidly exchanged and epimerized into dimer **2b**, and acyclic dimer **3a** was converted quantitatively into hexadeuterio **2a** under the deuterium-exchange conditions (refluxing deuterioethanol–sodium methoxide for *ca.* 5–10 min). Trimer **4** was readily destroyed under these reaction conditions. However, a low yield of a sample was recovered after 5-min heating on the steam bath, mp 138–140°, which contained deuterium; almost complete exchange of hydrogen for deuterium of the C-6 ring methylene protons (d, τ 7.18), and side-chain methylene protons (multiplets at τ 7.83 and 8.25) occurred, as evidenced by the disappearance of these peaks in the recovered sample; the remaining enolizable protons were incompletely exchanged.

3,5-Diphenyl-2-isopropyl-2-cyclohexen-1-one (7).—To styryl isobutyl ketone (18.8 g, 0.10 mol) and acetophenone (12.0 g, 0.10 mol) dissolved in 100 ml of absolute ethanol was added a solution of sodium ethoxide prepared from 0.46 g of sodium dissolved in 15 ml of absolute ethanol. The solution was allowed to stand at 25° for 17 hr, then heated under reflux for 24 hr. The red-orange solution was neutralized with acetic acid and concentrated to dryness. The gummy residue was extracted with methylene chloride and the extracts were concentrated to yield 22.8 g of viscous red oil; crystallization from ethanol gave 1.24 g of crude cyclic dimer **2a**, mp 175–195°. The filtrate was distilled to yield 1.0 g of recovered acetophenone. The residue (19.7 g) was crystallized from hexane–cyclohexane to yield 2.0 g of additional **2a**, mp 170–200°. The filtrate was concentrated and the residue dissolved in benzene containing 0.1 g of camphorsulfonic acid; the solution was then heated under reflux for 16 hr. The solution was concentrated and the residue dissolved in hot hexane, treated with decolorizing charcoal (Darco G-60), filtered, and cooled to −15°. The gummy crystals (4.62 g) which were deposited were fractionally crystallized from hexane to yield 0.50 g of cyclohexenone **7**: mp 88–90°; recrystallization from hexane raised the melting point to 90–91°; $\nu_{KBr}^{cm^{-1}}$ 1640 (C=O), 1600 (C=C); λ_{max}^{EtOH} 204 mμ (ε 17,900), 260 (9800).

Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64; mol wt, 290.4. Found: C, 87.20; H, 7.60; mol wt, 321 (vapor osmometry).

3,5-Diphenyl-2-isopropyl-4-(3-methylbutanoyl)phenol (5).—A 0.4-g sample of cyclic dimer **2b** and 0.05 g of 10% palladium–charcoal were mixed and heated in a nitrogen atmosphere at 280–290° for 15 min, and at 300–310° for 5 min. The cooled residue was extracted with methylene chloride and the filtrates were concentrated to yield 0.37 g of residue which was crystallized from ethanol to yield 80 mg (20%) of dimer **2a** as long needles, mp 200–203° (when mixed with an authentic sample of **2a** the melting point was not depressed). No **2b** could be recovered. The filtrate was concentrated to dryness and the residue crystallized from benzene to yield 20 mg (5%) of crude **5**, mp 190–200°; recrystallization gave **5**, rhombic prisms, mp 200–201°; when mixed with an authentic sample, mp 202–203°, the melting point was not depressed (lit.[9c] mp 202–203°).

3,5-Diphenyl-2-isopropylphenol (6).—A mixture of 1.0 g of 3,5-diphenyl-2-isopropyl-2-cyclohexen-1-one (**7**) and 0.3 g of 10% palladium on charcoal was heated under gentle reflux in a nitrogen atmosphere for 10 min. The mixture was extracted with hot chloroform, filtered, and the filtrate concentrated to dryness. Crystallization of the residue from hexane gave 0.44 g (44%) of crude phenol **6**, mp 105–108°. Recrystallization from hexane gave needlelike prisms: mp 111–114° (lit.[9c] mp 114–115°); when mixed with an authentic sample, mp 114–115°, the melting point was not depressed; λ_{max}^{EtOH} 206 mμ (ε 38,000), 235 (27,000), 264 (16,500), 300 (4450).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.57; H, 7.05.

Registry No.—**1**, 2892-18-4; **2a**, 18346-83-3; hexadeuterio **2a**, 18366-75-1; **2b**, 18346-82-2; hexadeuterio **2b**, 18366-76-2; **2c**, 18366-77-3; **3a**, 10596-48-2; **4**, 18366-78-4; **6**, 18354-80-8; **7**, 18354-81-9.

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Photorearrangement of β,γ-Unsaturated Ketones. Application to the Synthesis of Bridged Bicyclic Ketones

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Ultraviolet irradiation of β,γ-unsaturated ketones such as **3**, **5**, and **7** in which the double bond occupies an exocyclic position with respect to the carbonyl group has been found to give rise exclusively to unsaturated bridged bicyclic ketones. The photorearrangements were shown to be completely reversible, the apparent photostationary states lying substantially in favor of **3**, **5**, and **7**. Although ketones **4**, **6**, and **8** do not predominate at equilibrium, isolation can be achieved by preparative-scale gas chromatography. These conversions therefore provide synthetic entry to previously unknown and otherwise difficultly accessible carbonyl compounds. The spectra and physical properties of these ketones are presented in some detail.

Light-induced transformations of β,γ-unsaturated ketones have been the subject of recent intensive study. The capability of such formally nonconjugated molecules for photochemical excitation and subsequent chemical change is linked to the enhanced $n \rightarrow \pi^*$ absorption generally associated with the β,γ-unsaturated carbonyl chromophore.[2] In brief, it is now recognized that cyclic and acyclic β,γ-unsaturated ketones may undergo three general types of phototransformation depending upon the structure of the

(1) The Ohio State University Postdoctoral Fellow, 1967–1968.

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