vel.[15] The isoheptyl bromide[16] was obtained in 90% yield and distilled at 84–85° (45 mm) [lit.[14] 83° (45 mm)].

The Grignard reagent from 1 mol of isoheptyl bromide was prepared and treated with allyl bromide according to the directions of Vogel.[17] The product, 8-methyl-1-nonene, was distilled in a ten-plate column at 170–171°. No impurities could be detected in the product by glpc analysis. *Anal.* Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.36; H, 14.41.

Alkylation of Benzene with 8-Methyl-1-nonene.—All the alkylation reactions have been described previously.[4,5] The crude akylbenzenes were analyzed by glpc before distillation to avoid any discrepancy due to the fact that the internal alkylbenzenes tend to have slightly lower boiling points than the ones near the end of the chain. The chromatograph used was an F & M Model 810 equipped with a recorder and an Infotronics digital readout system. The stainless steel column was 200 ft × 0.01 in. and was coated with OV7.[18] The crude products were then distilled in a ten-plate column, and the fraction boiling at 100–108° (2 mm) ($n^{25}\text{D}$ 1.4810) was collected. The yields and isomer distributions appear in the table.

Registry No.—1, 26741-24-2; benzene, 71-43-2.

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(15) O. Kamm and C. S. Marvel, ref 13, p 30.

(16) A recent investigation of the reaction of alcohols with hydrobromic acid showed that primary alcohols do not undergo isomerization during the reaction: W. Gerrard and H. R. Hudson, *J. Chem. Soc.*, 2310 (1964).

(17) I. Vogel, "Practical Organic Chemistry," Wiley, New York, N. Y., 1961, p 240.

(18) This is 20% phenyl-substituted methyl silicone available from Supelco, Inc., Bellefonte, Pa. 16823.

The Base-Catalyzed Condensation of Acetophenone and Isobutyraldehyde. A Reexamination of the Monomeric and Dimeric Adducts

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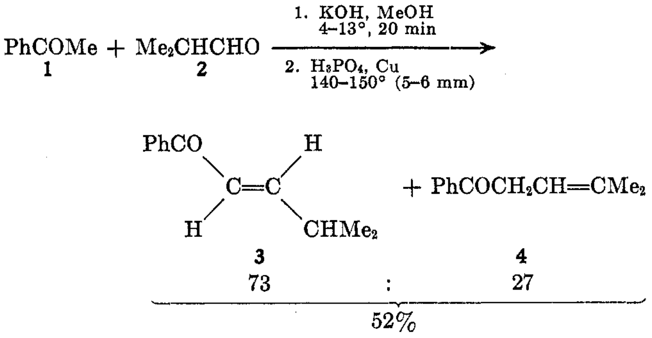
The base-catalyzed condensation of acetophenone (1) and isobutyraldehyde (2) at 4–13° followed by dehydration at 140–150° with phosphoric acid and copper gave a 73:27 mixture of 1-phenyl-4-methyl-*trans*-2-penten-1-one (3) and 1-phenyl-4-methyl-3-penten-1-one (4). Condensation of 1 and 2 at 55° gave both diastereomers of 3-isopropyl-2-(2-methylpropenyl)-1,5-diphenyl-1,5-pentanedione (5 and 6) and a ~70:30 mixture of 4 and 3. Heating the high-melting diastereomeric dimer 5 with sodium acetate at 170–200° gave a 72:28 mixture of 4 and 3. Attempted equilibration of 3 and 4 with potassium hydroxide in methanol gave rapid conversion of the conjugated isomer 3 to 1-phenyl-3-methoxy-4-methyl-1-pentanone (10) followed by a slower reaction of 3, 4, and probably 10 to give the dimers 5 and 6. This paper clarifies some earlier reports on the products of the base-catalyzed condensation of 1 and 2.

The base-catalyzed condensation of acetophenone (**1**) and isobutyraldehyde (**2**) (and dehydration) under a variety of conditions has been reported to give either the α,β-unsaturated ketone **3** (stereochemistry unspecified)[1–5] and/or the dimer **5** (stereochemistry unspecified).[3,6] The dimer **5** on heating with sodium acetate reportedly gave the ketone **3**.[3] During the course of some other work we had need of the ketone **3**, which we set out to prepare by the methods described above. It became apparent very soon after our work was initiated that most of the literature reports of the synthesis of **3** were partially in error. This paper describes our work on the unraveling of the major processes which occur during the reaction of acetophenone (**1**) and isobutyraldehyde (**2**) in the presence of base, and on some of the subsequent transformations of the products of these reactions.

Results

The low-temperature base-catalyzed condensation of acetophenone (**1**) and isobutyraldehyde (**2**) and subsequent dehydration were carried out according to the procedure of Stanishevskii and Tishchenko.[5] The exact details of part of the process were not reported by these authors. In addition to the reported product **3** (determined to be mainly trans), an appreciable amount of the unconjugated isomer **4** also was obtained (73:27 ratio, 52% yield). A small amount (≤5% of **3**) of the cis isomer **7** of **3** may have been formed (see Experimental Section). The structure proof of both isomers **3** and **4** will be presented below.



The high-temperature condensation of the ketone **1** with the aldehyde **2** was carried out as described by Kulka and coworkers.[3] In addition to the high-melting dimer **5**, another lower melting dimer **6** also was isolated. On the basis of nmr data which are described below, these dimers tentatively have been assigned the diastereomeric structures reported by Anet.[6] After the addition of sodium acetate a small amount of the monomers **3** and **4** could be distilled from the reaction mixture, but the major isomer was the unconjugated one, **4**. Kulka and coworkers[3] reported the isolation of the high-melting dimer in 60% yield and the conjugated monomer **3** in 22% yield.

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(1) H. Thoms and H. Kahre, *Arch. Pharm.* (*Weinheim*), **263**, 241 (1925).

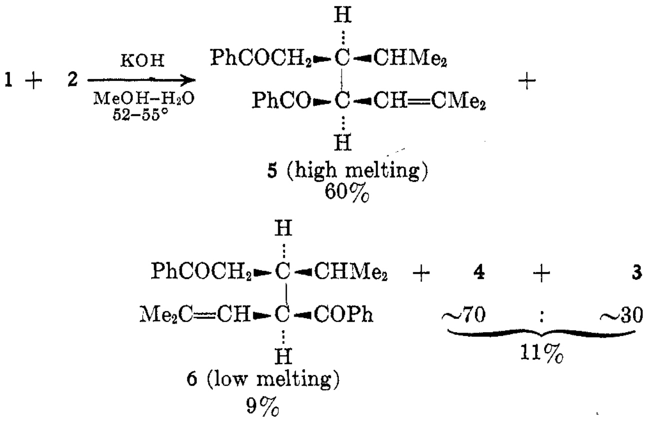
(2) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739 (1957).

(3) K. Kulka, R. J. Eiserle, J. A. Rogers, Jr., and F. W. Richter, *J. Org. Chem.*, **25**, 270 (1960).

(4) R. A. Rao and R. R. Rao, *Indian J. Chem.*, **4**, 280 (1966); *Chem. Abstr.*, **65**, 13623 (1966).

(5) L. S. Stanishevskii and I. G. Tishchenko, *Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk*, 123 (1967); *Chem. Abstr.*, **67**, 32422 (1967).

(6) R. Anet, *J. Org. Chem.*, **26**, 246 (1961).



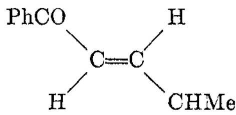
The high-melting dimer was converted to essentially the same mixture of monomers as obtained in the preceding experiment by heating under vacuum with sodium acetate as described by Kulka and coworkers.[3]

$$\mathbf{5} \xrightarrow[170\text{–}200°,\ 10\ \text{mm}]{\text{NaOAc}} \underbrace{\overset{\mathbf{4}}{72} \; \overset{+}{:} \; \overset{\mathbf{3}}{28}}_{91\%}$$

A trace amount (~5% of **3**) of the cis isomer **7** may have been formed.

Although the monomers **3** and **4** were not isolated in pure form, samples of greater than 70% purity of each isomer were available from the above reactions, making it possible to determine some nmr and infrared spectral data for each. The impurity in each case was the other isomer. The isomeric monomers were not separable on a silicone rubber gas chromatographic column. Mixtures of the two could be analyzed conveniently by nmr spectroscopy. Mass and ultraviolet spectra were also determined on the mixtures. The spectral details are given in the Experimental Section. We note here the most significant features which serve to define the structures.

The nmr spectrum of the conjugated isomer **3** exhibited a one-proton doublet of doublets (J = 15.6 and 5.1 Hz) at −7.08 ppm and a one-proton doublet (J = 15.6 Hz) at −6.74 ppm for the olefinic protons. The common coupling constant, 15.6 Hz, is reasonable for the trans stereochemistry. The cis isomer **7** would be expected to have a vicinal olefinic coupling constant of 11–12 Hz based on the model compounds **8** and **9**.[7,8]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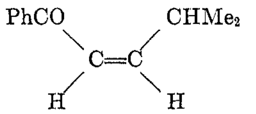
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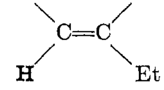
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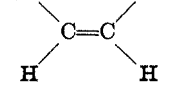
J_{trans} = 15.6 Hz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J_{cis} = 11.5 Hz

The nmr spectrum of **3** also exhibited a one-proton multiplet at −2.5 ppm for the methine proton and a six-proton doublet split 6.7 Hz by the methine proton at −1.11 ppm for the two equivalent methyl groups. In each sample of the monomers a weak doublet also was observed at −1.04 ppm with a 6.7-Hz coupling constant. The relative areas of the doublets at −1.11 and −1.04 ppm were ~95:5, respectively. These two doublets may be due to the trans (**3**) and cis (**7**) isomers, respectively. The olefinic proton resonances of **7** could not be detected. The nmr spectrum of the unconjugated isomer exhibited a one-proton triplet with further fine structure at −5.44 ppm coupled by 7.0 Hz to the methylene group, which appeared as a two-proton doublet at −3.65 ppm. The two nonequivalent vinylic methyl groups appeared mainly as singlets with small splittings at −1.74 and −1.68 ppm. The aromatic region of the spectrum of each monomer **3** and **4** had the typical benzoyl pattern.

The infrared spectrum of the conjugated isomer **3** had a carbonyl stretching band at a frequency, 1675 cm⁻¹, slightly lower than that of the unconjugated isomer **4**, 1695 cm⁻¹. The carbon–carbon double bond absorption was much more intense,[9] 1630 cm⁻¹, for the conjugated isomer **3**, than for the unconjugated isomer **4**. This band in **4** is probably at 1635 cm⁻¹, but there were several medium-intensity bands in this region which made this assignment tenuous.

The mass spectrum of each mixture (Table I) confirmed the monomeric character of each isomer **3** and **4**. In addition several features of these spectra were consistent with the assigned structures. The more highly conjugated isomer **3** gave the more intense molecular ion peak.[10] Isomer **3**, which contains an isopropyl group, gave more intense ion peaks for the loss of this fragment, m/e 131, and for that fragment, m/e 43. The loss of a phenyl group from the molecular ion, m/e 97, of isomer **3** leaves a more stable ion, $Me_2CHCH{=}CHCO^+$, than the corresponding ion from the other isomer **4**, $Me_2C{=}CHCH_2CO^+$.

TABLE I

MASS SPECTRA OF MIXTURES OF KETONES **3** AND **4**[a]

	Rel intensity		
m/e	73% **3** + 27% **4**	72% **4** + 28% **3**	Assignment
174	21.8	9.6	M^+
159		3.1	$M^+ - CH_3$
145	2.6		$M^+ - C_2H_5$
131	2.6		$M^+ - C_3H_7$
116	3.2		$M^+ - C_3H_6O$ or C_4H_{10}
115	3.9		$M^+ - C_3H_7O$ or C_4H_{11}
105	100.0	100.0	$PhCO^+$
97	5.1	1.5	$M^+ - Ph$
91	3.9		$C_7H_7^+$
81	1.9		$CH_2{=}CHCH{=}CHCO^+$
77	34.6	46.5	Ph^+
69	2.6	2.7	$Me_2CHCH{=}CH^+$
55	1.9		$C_4H_7^+$
53	2.6	2.3	$C_4H_5^+$
51	10.9	9.2	$C_4H_3^+$
50	3.2		$C_4H_2^+$
43	4.5	1.5	$C_3H_7^+$ or CH_3CO^+
41	12.2	9.6	$C_3H_5^+$
39	5.1	3.9	$C_3H_3^+$

[a] Direct probe sample introduction, 40°.

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(7) P. Laszlo and P. v. R. Schleyer, *Bull. Soc. Chim. Fr.*, 87 (1964).

(8) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, pp 301–302.

(9) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 147.

(10) F. W. McLafferty, "Interpretation of Mass Spectra, An Introduction," W. A. Benjamin, New York, N. Y., 1966, p 212.

TABLE II

DESCRIPTION OF 100-MHz PROTON NMR SPECTRA OF DIMERS 5 AND 6[a]

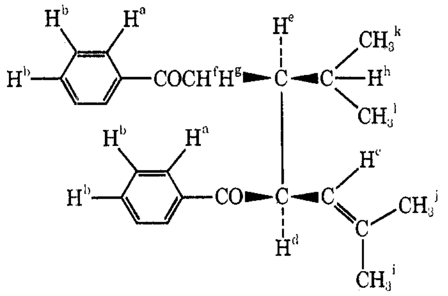
Absorption	Center, ppm 5[b]	6	Number of protons	Description[c]
H^a	−7.95		4	m
		−7.95	4	m
H^b	−7.45		6	m
		−7.45	6	m
H^c	−5.016 (−5.03)		1	d (10.5 Hz) of m (1.3 Hz)
		−5.209	1	d (10.2 Hz) of m (~1.4 Hz)
H^d	−4.392 (−4.4)		1	d (10.5 Hz) of d (8.9 Hz)
		−4.520	1	d (10.2 Hz) of d (7.4 Hz)
H^e	−3.15			
		−2.77	3 (5)	5, complex
H^f	−3.05		3 (6)	6, X_2Y appearance with Y further split, "J" ≅6 Hz
		−3.00[d]		
H^g	−2.75			
		−3.00[d]		
H^h	−1.777 (~−1.9)		1	m (7 Hz) of d (3.4 Hz)
		−1.951	1	m (7 Hz) of d (3.4 Hz)
H^i	−1.663 (−1.66)		3	d (1.3 Hz)
		−1.663[e]	3	d (1.35 Hz)
H^j	−1.354 (−1.40)		3	d (1.3 Hz)
		−1.663[e]	3	d (1.35 Hz)
H^k	−0.949 (−1.1)		3	d (6.9 Hz)
		−0.920	3	d (6.9 Hz)
H^l	−0.869 (−1.0)		3	d (6.9 Hz)
		−0.870	3	d (6.9 Hz)

[a] Solutions were 10% (w/v) in $CDCl_3$ with internal Me_4Si as shift reference. [b] Data (for $CDCl_3$ solution) reported by Anet[6] given in parentheses. [c] d = doublet, m = multiplet (≥5 lines). [d] These features are superimposed in $CDCl_3$ solution and separate upon addition of Eu(fod)$_3$. [e] These features are superimposed in $CDCl_3$ solution and separate upon addition of Eu(fod)$_3$.

The ultraviolet spectra of the two isomer mixtures also served to confirm the structures. The sample rich in the conjugated isomer **3** exhibited both π → π* and n → π* band maxima at longer wavelengths than did the sample rich in the nonconjugated isomer **4**.

The mass spectra of the dimers **5** and **6** confirmed their molecular weights and were generally consistent with the assigned structures.

The diastereomeric structures of **5** and **6** (erythro and threo, respectively) were assigned on the basis of their nmr spectra. Spectral features observed in deuteriochloroform solution at 100 MHz are described in Table II. The data (60 MHz) reported by Anet[6] for the high-melting isomer **5** are also shown for comparison.



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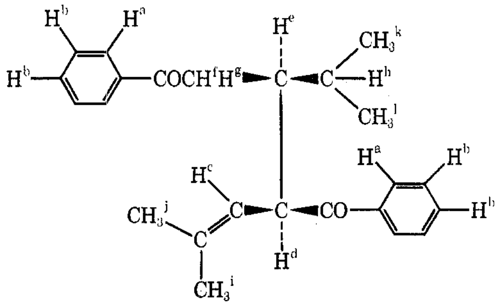

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TABLE III

APPARENT COUPLING CONSTANTS AT 100 MHz[a]

Protons coupled	Coupling constant, Hz 5[b]	6	Assignment
cd	10.5 (10)	10.2	Vicinal, trans or cis
ci	1.3 (1.5)	1.35	Long range, $CH_3C{=}CH$
cj	1.3 (1.3)	1.35	Long range, $CH_3C{=}CH$
de	8.9 (8.75)	7.4	Vicinal
ef	7.6[c]	5.0[c]	Vicinal
eg	5.0[c]	5.8[c]	Vicinal
eh	3.4	3.4	Vicinal, gauche
fg	17.6[c]	17[c]	Geminal
hk	6.9 (7.2)	6.9	Vicinal
hl	6.9 (7.2)	6.9	Vicinal

[a] Solutions were 10% (w/v) in $CDCl_3$. [b] Data (for $CDCl_3$ solution) reported by Anet[6] given in parentheses. [c] Obtained from 60-MHz spectrum with Eu(fod)$_3$ added.

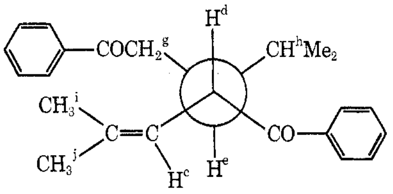
Spin–spin coupling among the protons was determined by selective decoupling experiments. Complete decoupling was performed in all cases. The relative signs of the coupling constants were not sought, because the net behavior is typical of the anticipated vicinal and geminal placements. The apparent values of the coupling constants are listed in Table III. It is apparent that the structures of **5** and **6** must be very similar. The chemical shifts of the protons and the couplings among them are fully consistent with the gross structures of **5** and **6**. Based on the concept of least nonbonded steric repulsions the conformations **5a** and

TABLE IV

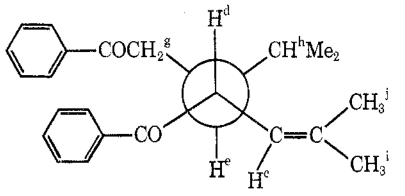
PARAMAGNETIC SHIFTS AT 60 MHz INDUCED BY ADDITION OF Eu(fod)$_3$ IN CDCl$_3$

	5				6			
	Chemical shift, Hz[a]		Δ (change), Hz	Rel effect, $100\Delta/\Sigma_c^l\Delta$	Chemical shift, Hz[a]		Δ (change), Hz	Rel effect, $100\Delta/\Sigma_c^l\|\Delta\|$
Proton	Initial	+Eu(fod)$_3$			Initial	+Eu(fod)$_3$		
c	301	531	230	15.7	313	314	1	0.1
d	262	429	167	11.4	270	342	72	10.0
e	191	641	450	30.7	165	$36\overline{3}$	$9\overline{8}$	13.5
f, g	175	344	169	11.5	180	300[b]	220	30.4
h	105	200	95	6.5	117	143	26	3.6
i	99.5	164	64.5	4.4	99.5	121	21.5	3.0
j	72	111	39	2.7	99.5	95	−4.5	−0.6
k	57	96	39	2.7	54	85.5	31.5	4.4
l	52.5	97	44.5	3.0	52.5	81.5	29	4.0
a	477	556, 567	80, 90	5.5, 6.1[c]	477	538	61	8.8[c]
b	448	468	20	1.4[c]	448	456	8	1.2[c]

[a] Downfield from internal Me$_4$Si. [b] Center of both lines which had separated. [c] On same relative scale as c–l.



5a



6a

6a are probably the predominant rotational isomers wherein protons H^d and H^e are trans; H^e and H^h are gauche; and H^c and H^d are cis or trans.

The only large difference between the spectra of the two isomers **5** and **6** lies in the relatively high shielding of one of the vinylic methyl groups of isomer **5**, H^j, tentatively assigned as the methyl group which is cis to the olefinic proton H^c. This shielding can occur if the methyl group is situated above the plane of a phenyl ring while the other methyl group, H^i, geminal to it is not. This is accomplished readily in the molecular conformation of **5a**, which satisfies the predominant conformational criteria of the preceding paragraph, with protons H^c and H^d being trans to each other. In this conformation, the methyl group, CH$_3$^{j}, can lie close to and directly over the far phenyl ring, PhCOCH$_2$–, while the methyl group, CH$_3$^{i}, trans to proton H^c, and H^c itself do not lie above this ring. In this conformation, also, it is possible to have the two carbonyl groups pointed unhindered in opposite directions and coplanar with their respective phenyl rings. This chemical shift difference between H^i and H^j in isomer **5** and their near equivalence in isomer **6** is the basis for making these tentative diastereomeric assignments.

The addition of the paramagnetic shift reagent Eu(fod)$_3$ to the deuteriochloroform solutions aided in confirming assignments of the CH$_2$CH systems because it shifted the three protons apart from one another, as well as shifting them downfield. Significant shifting of most other protons occurred also, and could serve as a basis for structure and conformation assignments when the origins of such shifts are understood well. Table IV gives nominal shifts of the various protons from internal tetramethylsilane at 60 MHz for original and shifted species. The greatest shifts occur for those protons which lie close to one or both carbonyl groups. The most dramatic difference between the isomers lies in the greater fractional deshielding change for the methyl groups H^i and H^j (H^i and H^j are not necessarily in the same relative positions in the two isomers) and protons H^c, H^e, H^f, and H^g. It appears that the differences reflect proximity of these protons to both carbonyl groups, with greater deshielding occurring when the protons are closer.

The infrared spectra of both dimers **5** and **6** were consistent with the assigned structures (see Experimental Section); each exhibited a carbonyl stretching band at 1680 cm^{-1}.

The ultraviolet spectra of the dimers **5** and **6** were nearly the same as that of acetophenone, in agreement with the proposed structures. As expected, the extinction coefficients (see Experimental Section) for the $\pi \rightarrow \pi^*$ bands of **5** and **6** were approximately twice that of acetophenone. Unexpectedly the $n \rightarrow \pi^*$ bands of the dimers **5** and **6** in hexane solution were approximately seven times as intense as that of acetophenone.

In an attempt to determine the equilibrium constant for the presumed prototropy of the conjugated **3** and unconjugated **4** ketones, each isomer mixture (0.1–0.9 *M*) was subjected to brief treatment with potassium hydroxide (0.1–1.0 *M*) in methanol. Extended treatment led to dimer **5** (and **6**) formation.[3] Instead of isomerization, the initial rapid reaction was addition of methanol, presumably to the conjugated isomer **3**, to give the methyl ether **10**. Dimer **5** and a small amount of dimer **6** were also formed at the longer reaction time. The results of these experiments are shown in Table V. Trace amounts of unidentified product(s) were also detected by nmr spectroscopy.

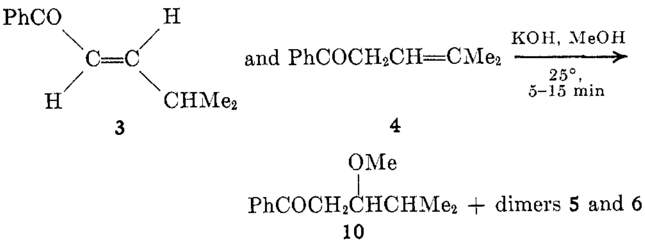


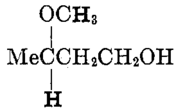
TABLE V

REACTIONS OF KETONES 3 AND 4 WITH POTASSIUM HYDROXIDE IN METHANOL AT 25°

Reaction no.	Time, min	Initial concn [**3** + **4**], M	Initial concn KOH, M[a]	Product composition, %[b] Ketone **3**[c]	Ketone **4**	Ether **10**	Dimer **5**[d]	Ratio of **3**:**4**	Material balance, %
e	0			75	25			75:25	100
1	5	0.097	0.10	41	20	39	~0	68:32	93
2	15	0.84	1.0	~20	~15	~35	~30	~60:40	~80
f	0			26	74			26:74	100
3	5	0.098	0.10	19	69	12	~0	21:79	95
4	15	0.85	1.0	~5	~50	~10	~30	~10:90	~90

[a] In methanol before addition of ketones **3** and **4**. [b] Compositions accurate to *ca.* ±2% for starting materials and reactions 1 and 3; *ca.* ±5–10% for reactions 2 and 4 (rounded to nearest 5%). [c] Possibly a trace of the cis isomer was present. [d] A small amount of the diastereomeric dimer **6** was also present. [e] Starting material for reactions 1 and 2. [f] Starting material for reactions 3 and 4.

The ether **10** was not isolated in pure form, but spectroscopic examination of reaction mixture 1 (Table V) left little doubt as to its identity. The mass spectrum showed ion peaks at m/e 206 (M^+), 191 ($M^+ - CH_3$), and 175 ($M^+ - CH_3O$). The nmr spectrum in deuteriochloroform solution exhibited a singlet at −3.30 ppm for the methoxy protons, a doublet (J = 6.7 Hz) at −0.95 ppm for the isopropyl methyl groups, a multiplet at −3.6 ppm for the methine proton, and a multiplet at −3.0 ppm due to the two methylene protons which are nonequivalent owing to the adjacent asymmetric center. The other expected peaks were obscured by the resonances from the ketones **3** and **4**. The chemical shifts for the methoxy and methine protons are in good agreement with those observed for the model compound **11** ($CDCl_3$ solution, -OCH_3 at



$$\mathrm{MeC(OCH_3)(H)CH_2CH_2OH}$$

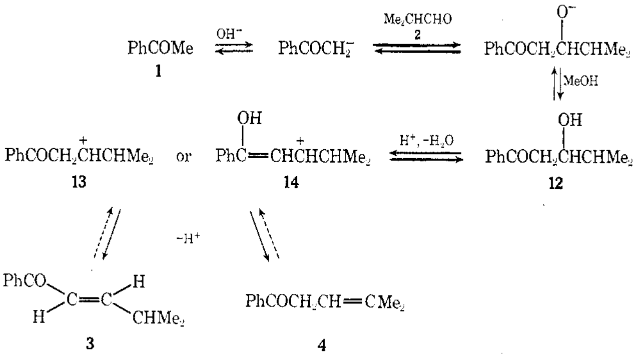
11

−3.33 and -OCH at −3.55 ppm).[11] The infrared spectrum of the ether **10** showed a CH stretching vibration for the methoxy group at 2835 cm^{-1} and a carbonyl stretching vibration at 1695 cm^{-1}.

Discussion

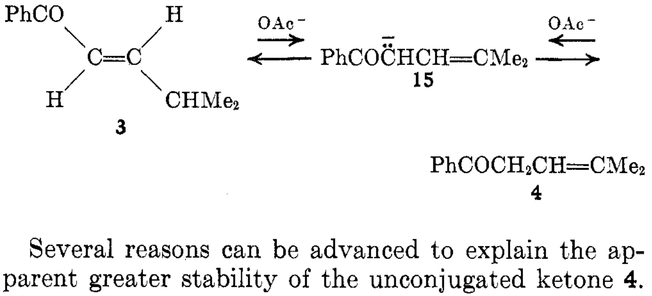
In the low-temperature condensation of acetophenone (**1**) and isobutyraldehyde (**2**), both the conjugated ketone **3** and the unconjugated isomer **4** presumably arise by acid-catalyzed (phosphoric acid and copper) dehydration of the intermediate ketol **12** (Scheme I).

SCHEME I



The ketones **3** and **4** may isomerize slightly under the reaction conditions, but the 73:27 ratio obtained in this reaction probably is not the equilibrium distribution, since other data (see below) indicate that the unconjugated isomer **4** probably is the more stable isomer. Thus the distribution of isomers **3** and **4** obtained in this reaction represents at least partial kinetic control. It seems reasonable that kinetic control in the proton loss from either cation **13** or **14** would favor formation of the conjugated ketone **3**. The kinetically more acidic protons in cations **13** and **14** undoubtedly are those α to the carbonyl and the hydroxylic proton, respectively.

In contrast to the above results, the base-catalyzed dedimerization of the dimer **5** gave predominantly the unconjugated isomer (72:28). We feel that this ratio probably is nearer the equilibrium distribution than is the ratio obtained in the dehydration reaction which followed the low-temperature condensation. The conjugated isomer **3** should predominate in the dedimerization if the products were stable under the reaction conditions. According to the probable mechanism for the dedimerization (Scheme II) the conjugated isomer should constitute greater than 50% of the product (50% plus the fraction of the enolate ion **15** which is protonated at the 4 position). Since the unconjugated ketone **4** is the predominant product, some of the conjugated isomer **3** must isomerize under the reaction conditions.



Several reasons can be advanced to explain the apparent greater stability of the unconjugated ketone **4**. First, the loss of conjugation energy in going from **3** to **4** is probably not so great as one might suspect, since the carbonyl group is already conjugated with the phenyl ring. The conjugation in **3** is only cross conjugation. Thus the loss is conjugation energy is less than a related aliphatic system would suffer. The unconjugated ketone **4** is a trisubstituted olefin while the conjugated isomer **3** is only a disubstituted olefin, a factor which favors isomer **4**. The cis isomer **7** would be expected to be less stable than **3** or **4** owing to excessive steric repulsion between the benzoyl and isopropyl groups.

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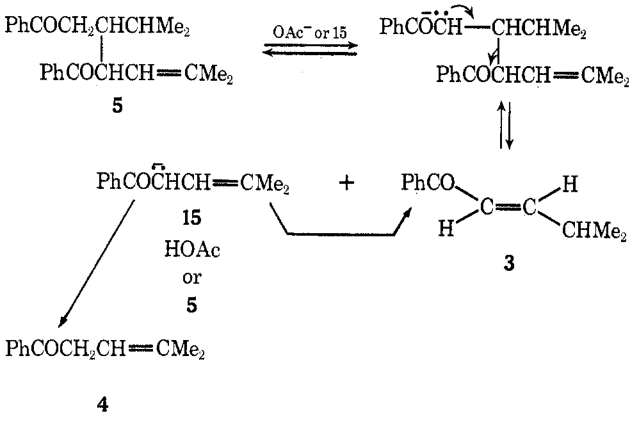
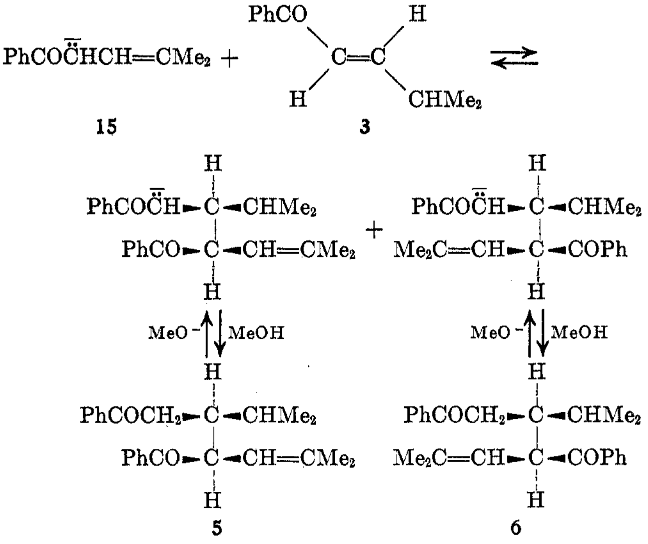
[11] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., National Press, 1962, No. 120.

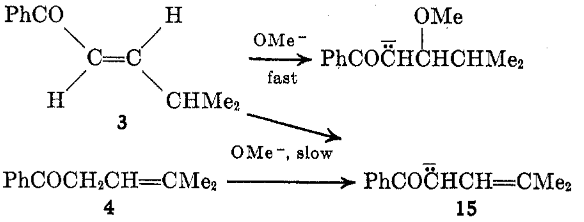
SCHEME II



SCHEME III



The attempt to determine the equilibrium constant between the ketones **3** and **4** in the presence of potassium hydroxide in methanol was thwarted by the rapid formation of the methyl ether **10**. From an examination of Table V it is apparent that the conjugated isomer **3** disappears much more rapidly than the unconjugated isomer **4**. Also, more ether **10** is formed from the unsaturated ketone sample which contains the higher concentration of **3**; the amount of ether **10** formed is roughly proportional to the initial concentration of isomer **3**. Thus the addition of methoxide ion to **3** is a faster reaction than is proton removal from either **3** or **4**. The methyl ether **10** appears to form rapidly and reach a steady concentration (Table V), while the dimers **5** and **6** form at a slower rate. The ether **10** probably is formed reversibly, thus accounting for the leveling off of the amount formed at higher conversions of the ketones **3** and **4**. The ether **10** is also likely formed in the condensation reaction of the ketone **1** and aldehyde **2** in methanol, but probably breaks down to the monomer **3**.



The enolate **15**, once formed, appears to undergo addition to the conjugated ketone **3** (Scheme III) more often than it reprotonates. The distribution of dimers **5** and **6** from the reactions in which dimer **5** precipitates from solution may not represent the thermodynamically controlled distribution, but may be a consequence of the less soluble dimer's (**5**) being removed from the reaction medium, thus shifting the equilibrium toward that isomer. Alternatively, although unlikely, the observed ratio could be the kinetically controlled distribution. In one experiment, Table V, no. 2, the dimer **5** did not precipitate, and the less soluble dimer **5** was again the major dimer formed. Thus the erythro dimer **5** is likely the more stable, assuming thermodynamic control. Based on estimated nonbonded repulsions one might predict conformer **5a** to be more stable than **6a**. Also the two highly dipolar carbonyl groups can be separated further in **5a** than in **6a**. Dimer **5a**, by the same argument as above, might be expected to be the major kinetically controlled product also.

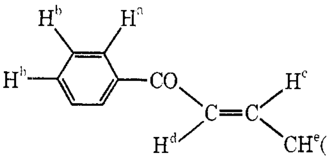
None of the reactions of the supposed conjugated ketone **3**, which were reported by previous workers as partial structure proofs, is incompatible with the actual material which these workers probably had in hand, namely a mixture of the ketones **3** and **4** and in some cases predominantly **4**. Catalytic hydrogenation of **4** would give the same products as from the supposed **3**.[3,4] Borohydride or Meerwein–Ponndorf–Verlay reduction of **4** would give an unsaturated alcohol which on catalytic hydrogenation and hydrogenolysis would give (4-methylpentyl)benzene, since the hydroxyl group would still be benzylic.[3] Ketone **4** is capable of undergoing base-catalyzed dimerization to **5**,[3a] as shown by our own experiments on the attempted equilibration of **3** and **4**. The infrared carbonyl absorptions for **3** and **4** are rather similar and could be mistaken for one another without both isomers in hand.[3]

The supposed synthesis of authentic ketone **3** reported by Kulka and coworkers[3] involving the Friedel–Crafts reaction of β-isopropylacrylyl chloride and the condensation of benzoylacetic acid and aldehyde **2** followed by decarboxylation are reactions which could easily lead to the unconjugated ketone **4** as well as **3**.

Experimental Section

General.—Melting points were taken in capillary tubes and were not corrected. Boiling points were not corrected. Elemental microanalyses were determined by Mr. L. E. Swim and coworkers. Infrared spectra were obtained by Mr. F. L. Beman and coworkers with a Perkin-Elmer 337 grating infrared spectrophotometer. Ultraviolet spectra were obtained by Mr. Beman and coworkers with a Perkin-Elmer 202 ultraviolet–visible spectrophotometer. Wavelengths were calibrated with the mercury arc lines at 253.7, 296.7, 313.2, and 365.0 mμ. The 60-MHz nmr spectra were obtained by Mr. Beman and coworkers with a Varian A-60 analytical spectrometer. All data reported are for 60-MHz spectra unless otherwise specified. The 100-MHz nmr spectra of the dimers **5** and **6** were obtained on 10% (w/v) chloroform-*d* solutions with a Varian HA-100 high-resolution spectrometer. Decoupling experiments were performed on this instrument. The spectra of **5** and **6** with Eu(fod)$_3$ [(t-BuCOCHCO-n-C_3F_7)$_3$Eu] added were obtained with a 60-MHz spectrometer. Mass spectra were obtained by Mr. J. H. Mark with an Atlas CH4B spectrometer which employed a direct probe sample introduction system. The molecular formulas assigned for various ion peaks are only tentative and have not been confirmed by high-resolution measurements. Gc analyses were carried out with a F & M 500 temperature-programmed gas chromatograph equipped with a thermal conductivity detector.

Low-Temperature Base-Catalyzed Condensation of Acetophenone (1) and Isobutraldehyde (2). Preparation of a 73:27 Mixture of 1-Phenyl-4-methyl-*trans*-2-penten-1-one (3) and 1-Phenyl-4-methyl-3-penten-1-one (4).—The general procedure of Stanishevskii and Tishchenko[5] was followed. Commercial isobutyraldehyde (40.4 ml, 32.1 g, 0.445 mol) was added to a stirred solution of commercial acetophenone (50.0 ml, 51.4 g, 0.428 mol) and potassium hydroxide (85.9% assay) (14.0 g, 0.21 mol) in 80 ml of methanol at 4–13° over a period of 15 min. The bright yellow solution was stirred for an additional 5 min, diluted with 175 ml of water, and neutralized with glacial acetic acid. The resulting mixture was extracted twice with methylene chloride (100, 50 ml), and the combined extracts were washed with water (3 × 50 ml). The methylene chloride was evaporated under vacuum, and 22.2 g of colorless liquid (probably acetophenone) was removed by distillation, bp 36–37.5° (0.6 mm). To the cooled distillation residue were added 85.7% phosphoric acid (4.89 g, 0.0428 mol) and copper powder (2.72 g, 0.0428 g-atom). The mixture was heated at 140–150° in a distillation pot connected to a 24-in. Vigreux column under vacuum. After a forerun of 2.85 g, a pale yellow liquid fraction (21.84 g, 29.3%, 52% based on unrecovered ketone **1**), bp 120–129° (5–6 mm) [lit. bp 101–102° (0.5 mm),[12] 130° (8 mm),[3] 136–137° (10 mm),[5] 146° (12 mm)[4]], $n^{25}\text{D}$ 1.5375 (lit[5] $n^{20}\text{D}$ 1.5390), was collected: $\nu_{\max}^{\text{CCl}_4}$ 3095 (w), 3070 (w), and 3040 (w) (ArH, =CH), 2970 (m), 2940 (m), and 2880 (m) (CH), 1695 (sh, m), 1675 (s, C=O of **3**), 1630 (s, C=C of **3**), 1455 cm^{-1} (m, CH_3); $\nu_{\max}^{\text{CS}_2}$ 1174 (m, *i*-Pr), 979 (m, *trans*-CH=CH), 693 cm^{-1} (s, Ph); $\lambda_{\max}^{\text{hexane}}$ (ϵ) *247.5*[13] (13,420, $\pi \rightarrow \pi^*$), 280 (sh, 1460), 315 (sh, 100), *340* (57, n $\rightarrow \pi^*$), 351 (sh, 54), 364 (sh, 45), 379 mμ (sh, 29); $\lambda_{\max}^{\text{MeOH}}$ (ϵ) 252 (13,160, $\pi \rightarrow \pi^*$), 333 (sh, 108, n $\rightarrow \pi^*$); nmr ($CDCl_3$) a multiplet at −8.1 to −7.8 (2.9 H relative area, H^a, $H^{a'}$), a multiplet at −7.6 to −7.1 with maxima at −7.50 and −7.46 (5.2 H, H^b, $H^{b'}$), an unsymmetrical doublet of doublets centered at −7.08 (low-field peaks partially obscured by H^b signal [H^c, J_{cd} = 15.6 Hz (assumed), J_{ce} = 5.1 Hz] incompletely resolved from an unsymmetrical doublet centered at −6.74 (H^d, J_{cd} = 15.6 Hz) (2.0 H total, H^d and high-field peaks of H^c), a multiplet (see below) at −5.44 (0.21 H, $H^{c'}$), a doublet (see below) at −3.65 (0.6 H, $H^{d'}$), a multiplet at −2.7 to −2.3 which consisted of at least five lines centered at ∼−2.5 (∼1.2 H, H^e), multiplets (see below) centered at −1.74 and −1.68 (2.5 H, $H^{e'}$), a doublet centered at −1.11 (6.0 H, H^f, J_{ef} = 6.7 Hz), a weak doublet centered at −1.04 ppm [J = 6.7 Hz, probably $-CH(C\mathbf{H}_3)_2$ of **7**, area ratio of doublets at −1.11 and −1.04 ∼>95:<5]. The ratio of isomers **3** and **4** was 73:27 based on the areas of the H^c, H^d, H^f, $H^{c'}$, $H^{d'}$, and $H^{e'}$ nmr signals. The distillation residue amounted to 19 g.



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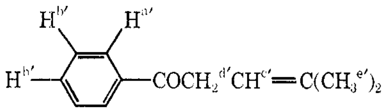

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High-Temperature Base-Catalyzed Condensation of Acetophenone (1) and Isobutyraldehyde (2). Preparation of Diastereomers of 3-Isopropyl-2-(2-methylpropenyl)-1,5-diphenyl-1,5-pentanedione (5 and 6).—This reaction was carried out in essentially the same manner as that reported by Kulka and coworkers.[3] Isobutyraldehyde (90.9 ml, 72.1 g, 1.00 mol) was added to a stirred mixture of acetophenone (117.3 ml, 120.7 g, 1.00 mol) and potassium hydroxide (85.9% assay) (17.0 g, 0.26 mol) in 125 ml of methanol and 125 ml of water at 52–55° over a period of 105 min. The bright yellow solution was stirred at this temperature for an additional 220 min, during which time a large amount of solid separated. After the reaction mixture stood at ∼25° for ∼16 hr, glacial acetic acid was added until the mixture was acidic. The solid was filtered and washed several times with methanol until colorless. The washings were combined with the filtrate, A, for processing later. The solid was air dried to give 103.7 g (60%) of white powder, mp 137–140°. The nmr, infrared, and ultraviolet spectra of this crude material were essentially identical with those of the purified sample of **5** described in the Results section and below. A 50.0-g portion was recrystallized twice from a 70:30 (v/v) mixture of methanol and benzene to give 34.0 g (40%) of the dione **5** as white needles: mp 142.5–143.5° (lit. mp 137.5°,[1] 139–140°,[2] 142–143°,[14] 144.5–145°[3]), $\nu_{\max}^{\text{Fluorolube}}$ 3065 (w, ArH), 2965 (m), 2930 (m), and 2875 (m) (CH), 1680 (s, C=O), 1455 cm^{-1} (m, CH_3); $\nu_{\max}^{\text{Nujol}}$ 753 (s) and 693 cm^{-1} (s, Ph); $\lambda_{\max}^{\text{hexane}}$ (ϵ) 240 (24,400, $\pi \rightarrow \pi^*$), 278 (sh, 1670), 286 (sh, 1160), 317 (sh, 206), 328 (253, n $\rightarrow \pi^*$), 338.5 (249), 354 (sh, 159), 372 mμ (sh, 44); $\lambda_{\max}^{\text{MeOH}}$ (ϵ) *244.5* (24,600, $\pi \rightarrow \pi^*$), 278 (sh, 3090), 287 (sh, 2020), 315 (sh, 344), *326.5* (373, n $\rightarrow \pi^*$), 336 mμ (sh, 342); mass spectrum (direct probe sample introduction, 115°) *m/e* (rel intensity) 41 (10.5, $C_3H_5^+$), 51 (6.8, $C_4H_3^+$), 69 (5.3, $Me_2C{=}CHCH_2^+$), 76 (36.3, $C_6H_4^+$), 105 (*100.0*, $PhCO^+$), 106 (10.5, $PhCO^+$ with one ^{13}C), 109 [5.0, $Me_2C{=}CHCH(CO)CH^+$, $M^+ - PhCOCH_2$, Ph, C_3H_7), 124 (40.8, $Me_2CHCH{=}CHCH{=}CMe_2^+$, $M^+ - PhCO$, $PhCOCH_2$], 174 (5.0, $PhCOCH{=}CHCHMe_2^+$), 175 (5.3, $PhCOCH_2C^+HCHMe_2$), 185 (5.1, $M^+ -$ $PhCOCH_2$, C_3H_7, H), 229 (2.4, $M^+ - PhCOCH_2$), 243 (4.5, $M^+ - PhCO$), 305 (2.6, $M^+ - C_3H_7$), 348 (1.6, M^+).

Partial evaporation of the solvent from filtrate and washings, A, gave a solid which was filtered and washed with methanol several times. The washings were combined with the filtrate, B, for processing later. The solid was air dried to give 15.7 g (9%) of white solid whose infrared and nmr spectra were essentially identical with those of the purified sample of dimer **6** described below. Recrystallization of an 8.0-g sample twice from methanol gave 4.6 g (5%) of fine white crystals of the dimer **6**: mp 84–85°; $\nu_{\max}^{\text{Fluorolube}}$ 3065 (w, ArH), 2970 (m), 2935 (m), 2915 (m), and 2880 (m) (CH), 1680 (s, C=O), 1455 cm^{-1} (m, CH_3); $\nu_{\max}^{\text{Nujol}}$ 749 (s) and 689 cm^{-1} (s, Ph); $\lambda_{\max}^{\text{hexane}}$ (ϵ) *241* (25,100, $\pi \rightarrow \pi^*$) 279 (sh, 1870), 288 (sh, 1270), *330* (253, n $\rightarrow \pi^*$), 337 (sh, 248), 353 (sh, 162), 371 mμ (sh, 43); $\lambda_{\max}^{\text{MeOH}}$ (ϵ) *244* (23,900, $\pi \rightarrow \pi^*$), 280 (sh, 2330), *326* (375, n $\rightarrow \pi^*$), 338 mμ (sh, 329); mass spectrum (direct probe sample introduction, 125°) *m/e* (rel intensity) 41 (5.8, $C_3H_5^+$), 51 (4.6, $C_4H_3^+$), 69 (4.0, $Me_2C{=}CHCH_2^+$), 76 (27.0, $C_6H_4^+$), 105 (*100.0*, $PhCO^+$), 106 (5.7, $PhCO^+$ with one ^{13}C), 109 [6.5, $Me_2C{=}CHCH(CO)CH^+$, $M^+ - PhCOCH_2$, Ph, C_3H_7], 124 (34.7, $Me_2CHCH{=}CHCH{=}CMe_2^+$, $M^+ - PhCO$, $PhCOCH_2$), 174 (4.4, $PhCOCH{=}CHCHMe_2^+$), 175 (3.9, $PhCOCH_2C^+HCHMe_2$), 185 (3.6, $M^+ - PhCOCH_2$, C_3H_7, H), 229 (2.3, $M^+ - PhCOCH_2$), 243 (2.2, $M^+ - PhCO$), 305 (3.2, $M^+ - C_3H_7$), 348 (1.1, M^+).

Anal. Calcd for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10; mol wt, 348. Found: C, 82.42, 82.56; H, 8.00, 8.09; mol wt, 348 (mass spectrometry).

The filtrate and washings, B, were evaporated at ∼35° (∼10 mm) to give 135.1 g of yellow oil. Most of the remaining solvent and unreacted starting materials **1** and **2** were removed by distillation (up to 75° head temperature at 25 mm). No monomer **3** or **4** could be obtained by further heating. To the yellow solid distillation residue was added 3 g of anhydrous sodium acetate. Distillation through a 24-in. Vigreux column gave 12.0 g of yellow liquid, bp 67° (10 mm)–139° (8 mm), whose nmr spectrum indicated the presence of acetophenone and acetic acid. A second pale yellow fraction, 15.5 g, bp 135–145° (9 mm), consisted of an approximately 70:30 mixture of the unconjugated ketone **4** and the conjugated ketone **3**, respectively, as determined by nmr and infrared analysis. Addition of more sodium acetate to the distillation residue, and continued distillation, gave another 4.1 g (total 19.6 g, 11%) of the 70:30 mixture of **4** and **3**, bp 126–129° (10 mm). No more distillate could be obtained with the pot temperature at 270°.

Dedimerization of High-Melting Diastereomer of 3-Isopropyl-2-(2-methylpropenyl)-1,5-diphenyl-1,5-pentanedione (5) with Sodium Acetate. Preparation of a 72:28 Mixture of 1-Phenyl-4-methyl-3-penten-1-one (4) and *trans*-1-Phenyl-4-methyl-2-penten-

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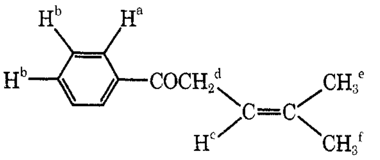
(12) N. M. Malenok and S. D. Kul'kina, *Zh. Org. Khim.*, **3**, 814 (1967); *J. Org. Chem. USSR*, **3**, 782 (1967).

(13) Italic value designates principal band in series.

(14) K. C. Brannock, R. D. Burpitt, and J. G. Thweatt, *J. Org. Chem.*, **28**, 1462 (1963).

1-one (3).—Essentially the same procedure as described by Kulka and coworkers[3] was used. A mixture of the high-melting dimer **5** (50.0 g, 0.143 mol) and anhydrous sodium acetate (1.5 g, 0.018 mol) was heated at 170–200° under vacuum in a distillation flask connected to a 24-in. Vigreux column. One fraction of slightly yellow liquid, 45.5 g (91%), was collected: bp 130° (8 mm)–144° (10 mm) [lit.[3] bp 130° (8 mm)]; n^{25}_{D} 1.5374 (lit.[3] n^{20}_{D} 1.5385); $\nu_{max}^{CCl_4}$ 3100 (w), 3075 (w), and 3045 (w) (ArH, =CH), 2980 (m), 2945 (m), 2925 (m), and 2885 (m) (CH), 1695 (s, C=O of **4**), 1680 (sh, m), 1665 (m), 1635 (m), 1605 (m), 1455 cm^{-1} (m, CH_3); $\nu_{max}^{CS_2}$ 747 (m) and 692 cm^{-1} (s, Ph); λ_{max}^{hexane} (ϵ) *241* (12,430, $\pi \rightarrow \pi^*$), 280 (sh, 1150), 288 (sh, 750), 316 (sh, 65), 327.5 (81), *339* (82, n $\rightarrow \pi^*$), 353 (sh, 62), 369 mμ (sh, 33); λ_{max}^{MeOH} (ϵ) 245.5 (12,160, $\pi \rightarrow \pi^*$) 321 mμ (sh, 134, n $\rightarrow \pi^*$); nmr ($CDCl_3$) a multiplet at −8.1 to −7.8 (3.0 H, H^a, $H^{a'}$), a multiplet at −7.6 to −7.2 with maxima at −7.50 and −7.47 (4.7 H, H^b, $H^{b'}$), a multiplet (see above) at −7.0 to −6.6 (0.7 H, $H^{c'}$, $H^{d'}$), a triplet of triplets centered at −5.44 with further ill-defined splitting (1.0 H, H^c, J_{cd} = 6.9 Hz, $J_{ce,cf} \cong$ 1.4 Hz), a doublet centered at −3.65 (1.9 H, H^d, J_{cd} = 6.9 Hz), a multiplet (see above) at −2.7 to −2.2 (0.35 H, $H^{e'}$), a doublet centered at −1.74 with further ill-defined splitting (H^e, J_{ce} = 1.1 Hz) incompletely resolved from a singlet at −1.68 with ill-defined splitting (H^f) (6.1 H total), a doublet (see above) at −1.11 (2.4 H, $H^{f'}$) and a weak doublet centered at −1.04 ppm (J = 6.7 Hz, area ratio of doublets at −1.11 and −1.04 ~95:5). The ratio of isomers **4** and **3** was 72:28 based on the areas of the H^c, H^d, H^e, H^f, $H^{c'}$, $H^{d'}$, $H^{e'}$, and $H^{f'}$ nmr signals. Gc analysis (2 ft × 0.25 in. column packed with 20% 410 silicone gum rubber on 60–80 mesh Chromosorb Z, column and injection port temperature 150°, He flow rate 48 ml/min) showed only one (>99.8% by area) major peak, retention time 5.8 min. The material did not elute from a 10-ft UCON column at 200°.



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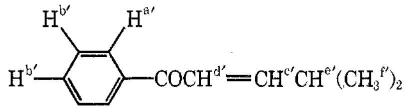
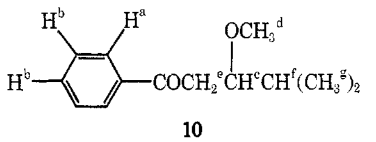


3

Attempted Equilibration of *trans*-1-Phenyl-4-methyl-2-penten-1-one (3) and 1-Phenyl-4-methyl-3-penten-1-one (4). A. Isomer 3 in 0.1 *M* Potassium Hydroxide for 5 Min. Characterization of 1-Phenyl-3-methoxy-4-methyl-1-pentanone (10).—A 0.1 *M* solution of methanolic potassium hydroxide was prepared by dissolving 6.53 g (85.9% assay, 0.100 mol) of potassium hydroxide in enough methanol to make 1 l. of solution. A portion (28.7 ml, 2.87 mmol of KOH) was purged with nitrogen for 10 min in a serum capped flask. A mixture of the isomeric ketones **3** and **4** (75 ± 2% **3**, 25 ± 2% **4**) (0.50 ml, 0.49 g, 2.8 mmol) was added in one portion at 25° to give a clear yellow solution (0.097 *M* ketones). The solution was allowed to stand at 25.0° in a water bath for 5 min. Water (25 ml) was added, and the resulting mixture was neutralized with glacial acetic acid. The neutral solution was extracted with methylene chloride (2 × 20 ml, 10 ml), and the combined extracts were washed with water (2 × 20 ml, 10 ml). After drying over anhydrous calcium sulfate the solvent was removed under vacuum to give 0.492 g of colorless oil. The nmr spectrum ($CDCl_3$) showed the peaks due to the ketones **3** and **4** and the methyl ether **10**, a low-intensity multiplet at −3.8 to −3.4 (H^e, partially obscured by the −3.65 ppm doublet of the ketone **4**), a high-intensity singlet at −3.30 (H^d), at least a four-line multiplet of medium intensity at −3.2 to −2.9 (H^e, no simple splitting pattern), and a high-intensity doublet centered at −0.95 ppm (H^g, $J_{fg} \cong$ 6.7 Hz). The relative intensities were in reasonable accord with the structure **10**. The resonances due to the other protons, H^a, H^b, and H^f, were obscured by the corresponding resonances for the ketones **3** and **4**. The molar ratio of products **3**, **4**, and **10** was 41:20:39, respectively, based on the peak areas at −6.8 (**3**), −5.4 (**4**), and −3.3 ppm (**10**). Essentially no dimers **5** and **6** were detected. The infrared spectrum (CCl_4) showed bands in addition to those due to ketones **3** and **4** at 2835 (OCH_3[15] of **10**), 1695 (more intense than in spectrum of starting mixture of ketones **3** and **4**, C=O of **10**), (CS_2) 1110 and 1091 cm^{-1} (CO[16]). The mass spectrum (direct probe sample introduction, 40°) showed ion peaks for the ketones **3** and **4**, and in addition showed significant peaks at *m/e* (rel intensity) 206 (0.4, M^+ of **10**), 192 (0.4, $M^+ - CH_2$), 191 (3.2, $M^+ - CH_3$), 176 (0.4, $M^+ - CH_2O$), 175 (1.1, $M^+ - CH_3O$), 172 (2.1, $M^+ - CH_3OH, H_2$), 163 (7.0, M^+ − CO, CH_3) [reference peaks, *m/e* 174 (7.0, $M^+ - CH_3OH$ and M^+ of **3** and **4**) and 105 (*100.0*, $PhCO^+$)].



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B. Isomer 4 in 0.1 *M* Potassium Hydroxide for 5 Min.—As in the preceding experiment, a mixture of the ketones **4** and **3** (74 ± 2% **4**, 26 ± 2% **3**) (0.50 ml, 0.50 g, 2.9 mmol) in 28.7 ml of the 0.1 *M* methanolic potassium hydroxide solution (0.098 *M* ketones) was allowed to react for 5 min at 25.0°. The resulting yellow solution was worked up as described in part A to give 0.485 g of colorless oil. Nmr analysis ($CDCl_3$) indicated a molar ratio of 19:69:12 of **3**, **4**, and **10**, respectively, based on peak areas at −6.8 (**3**), −5.4 and −1.7 (**4**), and −3.3 ppm (**10**). Essentially no dimers **5** and **6** were detected.

C. Isomer 3 in 1 *M* Potassium Hydroxide for 15 Min.—A 1 *M* solution of methanolic potassium hydroxide was prepared by dissolving 6.53 g (85.9% assay, 0.100 mol) of potassium hydroxide in enough methanol to make 100 ml of solution. A portion (2.87 ml, 2.87 mmol of KOH) was purged with nitrogen for 5 min in a serum capped vial. A mixture of the isomeric ketones **3** and **4** (75 ± 2% **3**, 25 ± 2% **4**) (0.50 ml, 0.49 g, 2.8 mmol) was added in one portion at 25° to give a brigh yellow solution (0.84 *M* ketones). The solution was allowed to stand at 25.0 ± 0.2° for 15 min. Water (3 ml) was added and the cloudy white mixture, which contained a white solid, was neutralized with glacial acetic acid. The neutral mixture was extracted with methylene chloride (2 × 2 ml, 1 ml). The solid dissolved in the methylene chloride. The combined extracts were washed with water (2 × 2 ml, 1 ml) and dried over anhydrous calcium sulfate. Evaporation of the solvent under vacuum gave 0.406 g of waxy white solid. Nmr analysis ($CDCl_3$) indicated a molar ratio of ~20:~15:~35:~30 (all ±5–10%) of **3**, **4**, **10**, and **5**, respectively, based on peak areas at −6.8 (**3**), −5.4 and −1.74 (**4**), −3.3 (**10**), and −5.0, −4.4, and −1.4 ppm (**5**). A trace (few per cent) of the dimer **6** was present as determined by shoulders in the −0.9 ppm region.

D. Isomer 4 in 1 *M* Potassium Hydroxide for 15 Min.—As described in part C above, a mixture of the ketones **4** and **3** (74 ± 2% **4**, 26 ± 2% **3**) (0.50 ml, 0.50 g, 2.9 mmol) in 2.87 ml of the 1 *M* methanolic potassium hydroxide solution (0.85 *M* ketones) was allowed to react for 15 min at 25.0 ± 0.2°. The solution had set up to a crystalline mass during this time. This mixture was worked up as described in part C to give 0.442 g of waxy white solid. Nmr analysis ($CDCl_3$) indicated a molar ratio of ~5:~50:~10:~30 (all ±5–10%) of **3**, **4**, **10**, and **5**, respectively, based on peak areas at −6.8 and −1.1 (low-field branch) (**3**), −3.7 (**4**), −3.3 (**10**), and −1.4 ppm (**5**). A trace (few per cent) of the dimer **6** was present as shown in part C.

Registry No.—**1**, 98-86-2; **2**, 78-84-2; **3**, 36597-08-7; **4**, 36597-09-8; **5**, 36597-10-1; **6**, 36597-11-2; **10**, 36597-12-3.

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(15) Reference 9, p 133.

(16) Reference 9, p 189.