

5 ml of alcohol was added, under nitrogen, a solution of 0.951 g (4.4 mmoles) of sodium metaperiodate in 5 ml of water. The resulting milky solution was stirred at room temperature for 1 hr and then diluted with water and extracted with several portions of ether. The combined ether solutions were washed with sodium thiosulfate solution and saturated sodium chloride solution. After drying and evaporation of solvent, distillation yielded 0.546 g (82%) of a colorless liquid, bp 59° (0.2 mm), with the infrared and nmr spectral characteristics of **5**, showing on capillary glpc at 80° one major peak at 39 min (99%) and no peak corresponding to **6**. (ii) In another run 0.602 g (2.36 mmoles) of adduct yielded 0.428 g of diol after reduction with lithium aluminum hydride. To this diol in 5 ml of acetic acid (distilled from chromic oxide) was added, with stirring under nitrogen, a suspension of 2.08 g (4.7 mmoles) of lead tetraacetate in 10 ml of acetic acid. The resulting solution was stirred at room temperature for 30 min and a few drops of glycerol were added to destroy the excess oxidant. Water was added and the mixture was extracted with several portions of pentane. The combined pentane solutions were washed with water, sodium bicarbonate solution, and water. After drying and evaporation of the solvent, distillation yielded 0.303 g (82%) of a colorless liquid with the infrared and nmr spectral characteristics of **5**, showing, on capillary glpc at 80°, one major peak at 33 min (99%) and no peak corresponding to **6**.

B. From 3 (R = CN).—A solution of 5.66 g of adduct in 80 ml of alcohol was added, with stirring under nitrogen, to a solution of 10.58 g of sodium borohydride in 150 ml of alcohol. After standing overnight the mixture was worked up, affording, after distillation, 3.59 g (90%) of a viscous liquid, bp 83–84° (0.5 mm), which solidified on cooling: mp 60–66°; nmr chemical shifts (CCl₄) at τ 6.1–6.4 (1 H), 7.2–7.6 (1 H), and 8.42 (3 H).

To a solution of 9.69 g (58.3 mmoles) of alcohol, obtained as above, in 1300 ml of acetone (distilled from potassium permanganate), cooled in ice-water, was added dropwise over 5 min, with stirring under nitrogen, 18 ml of Jones reagent (144 mequiv). The mixture was then diluted with 400 ml of water and enough sodium bisulfite solution was added to destroy the excess oxidant. Work-up yielded, after distillation, 7.26 g which showed, for the combined fractions, on glpc at 160°, three peaks at 10 min (75%), 13 min (15%), and 20 min (9%), corresponding to **5**,

starting material, and **6**, respectively. The three fractions collected from the distillation were (a) 2.85 g, bp to 85° (0.2 mm), showing peaks at 10 min (90%) and 13 min (10%); (b) 2.62 g, bp 85–87° (0.2 mm), showing peaks at 10 min (82%), 13 min (15%), and 20 min (3%); and (c) 1.79 g, bp 87–140° (0.2 mm), showing peaks at 10 min (40%), 13 min (24%), and 20 min (32%).

Material corresponding to the peak at 10 min was collected by preparative glpc and an analytical sample of **5** was thereby obtained: λ_{\max} 5.82 μ ; $\lambda_{\max}^{\text{EtOH}}$ 237 m μ (ϵ 270); nmr chemical shift at τ 8.29 (3 H).

Anal. Calcd for C₁₁H₁₆O: C, 80.44; H, 9.82. Found: C, 80.31; H, 10.00.

Upon addition of sodium hydroxide solution to a solution of **5** in alcohol in an ultraviolet cell, the absorption of **6**, λ_{\max} 247 m μ (ϵ 11,900), was rapidly established.

Orientation Ratios.—A solution of 212 mg of crude **5**, obtained as described from crude adduct **3** (R = CO₂CH₃), in 3 ml of methanol containing 2 drops of 10% potassium hydroxide solution, was boiled under nitrogen for 5 min. The solution was cooled, diluted with saturated sodium chloride solution, and extracted with several portions of ether. The combined ether solutions were washed with saturated sodium chloride solution and dried. Evaporation of solvent and short-path distillation of the residue at 0.4 mm from an oil bath at 85–90° afforded 195 mg (92% recovery) of a colorless liquid with the ultraviolet and nmr spectral characteristics of **6**, and showing, on capillary glpc at 80°, peaks at 61 min (98%) and 87 min (2%) corresponding to those for **6** and **7**, respectively. Material corresponding to each glpc peak was collected and identified by a comparison of spectral data with those from authentic **6** and **7**.¹⁵

Samples of crude **5** from the other Diels–Alder adducts were similarly isomerized and analyzed with the results shown in Table I.

A synthetic mixture of 19.7 mg of **6** and 18.7 mg of **7**, showing two peaks on glpc of 57.7 and 42.3%, was subjected to the isomerization procedure and subsequent work-up. Before distillation, 31.2 mg (82% recovery) of a slightly yellow oil was obtained showing two peaks on glpc of 57.6 and 42.4%. After distillation, 28.4 mg (74% recovery) of a colorless liquid was obtained showing two peaks on glpc of 57.5 and 42.5%.

Acylation. I. The Mechanisms of Enol Ester and 1,3-Diketone Formation in the Reaction of Ketone–Enol Systems with Acyl Halides

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Acylation of ketone–sodium amide systems with acid chlorides gave mixtures of enol esters and 1,3-diketones, with the ratio of products formed being dependent on reaction conditions. 1,3-Diketones were obtained in good yields by acylation of the ketones–base system with enol benzoates. Several enol benzoates were also shown to rearrange, in the presence of sodium amide (and absence of ketone), to give 1,3-diketones.

The acylation of ketones having an α -hydrogen atom with acid chlorides or acid anhydrides has been reported as a convenient preparation route to many 1,3-diketones.^{1–3} With acid chlorides, the condensation is usually effected by means of a basic reagent such as sodium amide; with acid anhydrides, a Lewis acid such as boron trifluoride is generally used. O-Acyl derivatives are formed in these reactions, but the conditions can be controlled so that favorable yields of 1,3-

diketones can be obtained. In contrast to this it has been reported^{4,5} that enolates from various unsymmetrical ketones and triphenylmethylpotassium react with acid anhydrides (and presumably acid chlorides) to give primarily O-acylated products. The isomeric 1,3-diketones were not detected in these experiments, even in trace amounts.

The specificity of the latter reaction system to give only esters together with reported synthesis of 1,3-diketones from, for example, the sodium amide–aliphatic ketone–acid halide reaction suggests that the formation of products is more complex than the simple,

(1) (a) C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 59 (1954); (b) D. S. Breslow and C. R. Hauser, *J. Am. Chem. Soc.*, **62**, 2385 (1940).

(2) (a) B. O. Linn and C. R. Hauser, *ibid.*, **78**, 6066 (1956); (b) R. Robinson and R. C. Shah, *J. Chem. Soc.*, 610 (1933); (c) J. Munch-Peterson and C. R. Hauser, *J. Am. Chem. Soc.*, **71**, 770 (1949); (d) K. Meisenheimer and K. Wiebezahn, *Ber.*, **54**, 3195 (1921).

(3) A. Haller and E. Bauer, *Compt. Rend.*, **153**, 145 (1912).

(4) (a) H. O. House and V. Kramer, *J. Org. Chem.*, **27**, 4146 (1962); (b) *ibid.*, **28**, 3362 (1963); (c) A. J. Parker, *Quart. Rev. (London)*, **16**, 163 (1962).

(5) (a) P. Z. Bedoukian, *J. Am. Chem. Soc.*, **67**, 1430 (1945); (b) I. V. Machinskaya, G. P. Smirnova, and V. A. Barkhash, *J. Gen. Chem. USSR*, **31**, 2390 (1960).

TABLE I
THE EFFECT OF MODE OF ADDITION AND REACTANT RATIOS ON CARBON *vs.* OXYGEN ACYLATION

Acylating agent	Reactants (relative mole ratios)		Mode of addition ^a	Product distribution, %			
	Carbanion	Ketone-base system		Enol ester (O acylation)	1,3-Diketone (C acylation)	Total yield, %	
		Enolate anion					
PhCOCl (1)	NaNH ₂ (2)	CH ₃ COCH ₃ (2)	X	21	79	42	
PhCOCl (2)	NaNH ₂ (1)	CH ₃ COCH ₃ (1)	Y	88	12	47	
PhCOCl (2)	None	CH ₃ COCH ₃ (1)	Y	0 ^b	0	0	
CH ₃ COCl (3)	NaNH ₂ (1)	CH ₃ COCH ₃ (1)	Y	82 ^c	18	39	
PhCOCl (1)	NaNH ₂ (2)	CH ₃ COCH ₂ CH ₃ (2)	X	15 ^d	85	64	
PhCOCl (2)	NaNH (1)	CH ₃ COCH ₂ CH ₃ (1)	Y	96	4	77	
PhCOCl (2)	None	CH ₃ COCH ₂ CH ₃ (1)	X	0	0	0	
PhCOCl (2)	NaNH ₂ (3)	CH ₃ CH ₂ COCH ₂ CH ₃ (3)	X	26 ^e	74 ^e	58	
PhCOCl (2)	NaNH ₂ (1)	CH ₃ CH ₂ COCH ₃ (1)	X	100	0	49	
PhCOCl (1)	None	CH ₃ CHCOCH ₂ CH ₃ (3)	X	0	0	0	
(CH ₃ CO) ₂ O (3)	NaNH ₂ (1)	CH ₃ CH ₂ COCH ₂ CH ₃ (1)	Y	100	0	41	
PhCOCl (1)	NaNH ₂ (3)	(CH ₃) ₂ CHCH ₂ COCH ₂ CH(CH ₃) ₂ (3)	X	67	33	33 ^f	

^a Method X is dropwise addition of acylating agent to the ketone-base (in ether) under nitrogen; method Y is the reverse procedure. ^b Heating the reaction mixture to reflux for several hours failed to give product, perhaps because of the low enol content of acetone, $1.5 \times 10^{-3}\%$ at 25° reported in F. W. Swamer and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 1352 (1950). ^c Products were recovered from hydrolyzed reaction mixture by repeated ether extraction. ^d The methyl and methylene esters are obtained but the *cis* and *trans* isomers, if present, were not resolved by the glpc column used. ^e 1,3-Diketone was reported in 66% yield by other workers² as the only product. ^f Reported in ref 2.

TABLE II
KETONE-ENOL ESTERS FROM ACYLATION IN THE PRESENCE OF ACID CATALYSTS

Ester ^a	Yield, %	Bp, °C (mm)	n_D^{25}	Formula	Anal., %			
					Calcd		Found	
					C	H	C	H
Enol benzoate of								
2-Propanone	46	100-103 (5.0)	1.5075	C ₁₀ H ₁₀ O ₂	74.05	6.22	74.1	6.3
1,3-Diphenyl-2-propanone	23	130-135 (0.7)	1.5675	C ₂₂ H ₁₈ O ₂	84.05	5.77	84.18	5.66
2-Butanone	49	114 (4.5)	1.5190	C ₁₁ H ₁₂ O ₂	74.79	6.86	74.81	6.93
3-Methyl-2-butanone	16	85-87 (1.0)	1.5154	C ₁₂ H ₁₄ O ₂	75.76	7.42	75.78	7.53
3,3-Dimethyl-2-butanone	10	82-83 (1.2)	1.5006	C ₁₃ H ₁₆ O ₂	76.44	7.90	76.50	7.81
2-Pentanone	51	75-76 (0.3)	1.5003	C ₁₂ H ₁₄ O ₂	75.76	7.42	75.68	7.30
3-Pentanone	38	92-94 (2.0)	1.5110	C ₁₂ H ₁₄ O ₂	76.76	7.42	75.52	7.20
4-Methyl-2-pentanone	41	97-98 (2.0)	1.5052	C ₁₃ H ₁₆ O ₂	76.44	7.90	76.28	7.88
4,4-Dimethyl-2-pentanone	24	88-89 (0.8)	1.5048	C ₁₄ H ₁₈ O ₂	77.03	8.31	77.20	8.45
5-Methyl-2-hexanone	45	115-118 (0.7)	1.5005	C ₁₄ H ₁₈ O ₂	77.03	8.31	76.87	8.11
Enol acetate of								
2-Butanone	15	48-50 (5.0)	1.4470	C ₁₆ H ₁₀ O ₂	63.15	8.85	63.3	9.01
3-Pentanone	26	50-53 (0.15)	1.4210	C ₇ H ₁₂ O ₂	65.50	9.44	65.6	9.30

^a Or mixture of isomeric esters. See Table III for isomer distribution.

one-stage mechanisms that have been proposed.^{4,6,7} For example, it has been suggested that the initially formed enol ester (from O-acylation of the enolate anion) could subsequently react with any carbanion present to give the 1,3-diketones which had been observed by other workers.⁴

It was of interest, then, to investigate the effect of reaction conditions on the acylation of a series of aliphatic ketones with acid chlorides.

The acylation of the ketone-base anion (formed from the reaction of the aliphatic ketone with sodium amide in anhydrous ether) was found to be sensitive to the molar ratio of acid halide (or anhydride) to ketone-base (see Table I). When the ketone-sodium amide reaction product was added to excess acid halide (so as to minimize or eliminate the possible formation of 1,3-diketones by an acylation involving the enol ester), enol esters were the major product. However, small but significant yields of 1,3-diketones were obtained for each ketone-sodium amide system. When the acid halide was added to excess ketone-sodium amide

reaction product, although the major product was now the 1,3-diketone, low yields of enol ester were obtained. With a more sterically hindered ketone, such as 2,6-dimethyl-4-heptanone, enol ester formation predominates. This is not unexpected, since increased hindrance in a substituted ketone tends to stabilize the vinyl alcohol (enol) structure.⁸ Therefore, these reactions were not as specific as those reported by other workers to give enol esters⁴ or to give 1,3-diketones.^{1,2,9}

Since it was possible to shift the ratio of enol ester 1,3-diketone formed by changing the molar ratio of ketone-base to acylating agent, the possible reaction of enol esters with ketone anions was examined. Studies of the C acylation of ketone carbanions with aromatic and aliphatic esters in the presence of acid catalyst have been reported.^{10,11} However, reactions between enol esters and ketone-base systems have apparently not been previously investigated. A series of enol esters was synthesized by treating benzoyl

(8) R. C. Fuson, D. H. Chadwick, and M. L. Ward, *ibid.*, **68**, 389 (1946); (b) *ibid.*, **67**, 386 (1945).

(9) F. C. Whitmore and D. I. Randall, *ibid.*, **64**, 1242 (1942).

(10) See Swamer and Hauser in footnote b of Table I.

(11) (a) E. A. Jeffery and D. P. N. Satchell, *J. Chem. Soc.*, 1876 (1962); (b) *ibid.*, 3002 (1963).

(6) C. R. Hauser, F. C. Frostick, and E. H. Man, *J. Am. Chem. Soc.*, **74**, 3231 (1952).

(7) F. G. Young, F. C. Frostick, J. J. Sanderson, and C. R. Hauser, *ibid.*, **72**, 3635 (1950).

TABLE III
 ACYLATIONS WITH ENOL BENZOATES TO GIVE 1,3-DIKETONES

Acylating agent, enol benzoate of	Ketone, carbanion of ^a	1,3-Diketone product	Yield, %
2-Propanone	2-Propane	PhCOCH ₂ COCH ₃	71
2-Butanone	2-Butanone	PhCOCH ₂ COCH ₂ CH ₃	42
3-Pentanone	2-Butanone ^b	PhCOCH ₂ COCH ₂ CO ₃	53
3-Methyl-2-butanone	3-Methyl-2-butanone	PhCOCH ₂ COCH(CH ₃) ₂	58
2-Pentanone	2-Pentanone	PhCOCH ₂ COCH ₂ CH ₂ CH ₃	66
3-Pentanone	3-Pentanone	PhCOCH ₂ (CH ₃)COCH ₂ CH ₃	14
4-Methyl-2-pentanone	4-Methyl-2-pentanone	PhCOCH ₂ COCH ₂ CH(CH ₃) ₂	63
3,3-Dimethyl-2-butanone	3,3-Dimethyl-2-butanone	PhCOCH ₂ COC(CH ₃) ₃	47

^a Ketone carbanions were prepared in diethyl ether under nitrogen from equimolar amounts of sodium amide and the corresponding ketone. Similar yields of diketones were obtained whether the enol benzoates were added to the ketone-base system or *vice versa*.
^b With the cross-acylation, approximately 5% yield of O-acylation product was obtained.

 TABLE IV
 PROPERTIES OF 1,3-DIKETONES FROM ACYLATION OR ENOL ESTER REARRANGEMENT

1,3-Diketones	Bp, °C (mm)	Mp, °C	n _D ²⁰	Enol color ^d	Color	Mp, °C	Formula	Copper chelate			
								Anal., %		Found	
								C	H	C	H
PhCOCH ₂ COCH ₃	98-100 (0.2)	58	...	Red-brown	Sea green	199	C ₂₀ H ₁₈ O ₄ Cu	62.3	4.70	62.2	4.73
PhCOCH(CH ₃)COCH ₃	Purple
PhCOCH ₂ COCH ₂ CH ₃	92-94 (1) ^a	...	1.5730	Red-brown	Sea green	135 ^b	C ₂₂ H ₂₂ O ₄ Cu	63.9	5.36	64.1	5.21
PhCOCH(Et)COCH ₃	Purple
PhCOCH ₂ COCH(CH ₃) ₂	116-120 (2) ^b	...	1.5800	Red	Dark green	152	C ₂₄ H ₂₆ O ₄ Cu	65.3	5.93	65.5	6.09
PhCOCH(CH ₃)COCH ₂ CH ₃	90-94 (1) ^c	...	1.5415	Purple	Dark green	189 ^f	C ₂₄ H ₂₆ O ₄ Cu	65.3	5.93	65.4	6.12
PhCOCH ₂ COCH ₂ CH ₂ CH ₃	86-90 (1) ^d	31	1.5750	Red	Dark gray-green	137	C ₂₄ H ₂₆ O ₄ Cu	65.3	5.93	65.2	6.00
PhCOCH(<i>n</i> -Pr)COCH ₃	Purple
PhCOCH(<i>i</i> -Pr)COCH ₃	Purple
PhCOCH ₂ COC(CH ₃) ₃	118-121 (1.5)	...	1.5650	Brown	Pale green	205	C ₂₆ H ₃₀ O ₄ Cu	66.4	6.43	66.5	6.46
PhCOCH ₂ COCH ₂ CH(CH ₃) ₂	110-113 (1)	...	1.5621	Red	Olive	102	C ₂₆ H ₃₀ O ₄ Cu	66.4	6.43	66.2	6.45
PhCOCH ₂ CO(CH ₂) ₃ CH ₃	183-186 (30) ^e	Red
CH ₃ COCH ₂ COCH ₃	138 (atm)	...	1.4520	Red-brown	...	127	C ₁₀ H ₁₄ O ₄ Ni	46.8	5.50	47.05	5.54
CH ₃ COCH(CH ₃)COCH ₃	77-79 (30)	Purple
CH ₃ COCH ₂ COCH ₂ CH ₃	154-155 (atm)	...	1.4525	Brown	Green	198	C ₁₂ H ₁₈ O ₄ Cu	49.9	6.25	49.9	6.31

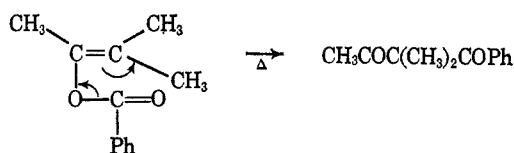
^a Bp 124.5° (5 mm) has been reported (ref 1, p 125). ^b Bp 186° (45 mm) has been reported [D. C. Nonhebel and H. D. Murdoch, *J. Chem. Soc.*, 2153 (1962)]. ^c Bp 134-135° (5.0 mm) has been reported. ^d Bp 166-171° (20 mm) has been reported (ref 1, p 124). ^e Reference 1, p 124. ^f C. R. Hauser and J. T. Adams, *J. Am. Chem. Soc.*, 66, 345 (1944). ^g Isomeric 1,3-diketones of the structure R₁COC(R₂R₃)COR₄ have not been considered, since they give no enol coloration with alcoholic ferric chloride and were precluded from the acylation products by choice of carbanion structure. ^h Reported by Nonhebel and Murdoch; see footnote b.

chloride with the ketone at reflux in the presence of trace amounts of *p*-toluenesulfonic acid (see Table II). Isomeric mixtures of enol esters were produced from those ketones where enolization was possible in more than one position and not structurally precluded. The enol esters were fractionated using gas-liquid partition chromatography and were characterized by their nmr and infrared spectra.¹² The purified enol esters were treated with stoichiometric amounts of ketone and sodium amide in diethyl ether under nitrogen at room temperature or with slight heating. 1,3-Diketones were produced in good yields in these reactions (Table III). Known and synthesized 1,3-diketones and their copper chelates (Table IV) were used to ascertain the molecular structures of the products from these reactions. When two enolizable positions were available on the parent ketone, thereby giving rise to the possibility of two products, the diketones were identified by the positive enol color of their ferric chelates: red for methyl acylated ketone,¹³ purple for acylation at a methylene site, and no color for methinyl-acylated ketone.^{14,15} Therefore, enol esters are good

acylating agents for carbanions derived from simple ketones, giving rise to good yields of 1,3-diketones.

Another potential contributing route to the formation of 1,3-diketones could be a base-catalyzed enol ester rearrangement. Rearrangements of this general type have been reported for enol esters treated with boron trifluoride-ether complex⁷ but not for base-catalyzed systems. It was found, however, that appreciable quantities of 1,3-diketones could be obtained by treating enol esters with sodium amide in diethyl ether at the reflux.

The mechanism by which the 1,3-diketones were obtained from enol esters in the presence of sodium amide (and absence of ketone) is, at present, not clear. A four-center intramolecular rearrangement involving the carbon-carbon double bond⁷ seems to be precluded, since an enol ester such as 3-methyl-2-butanone enol benzoate would be expected to give 1-phenyl-2,2-dimethyl-1,3-butanedione, whereas the product actually isolated from this rearrangement was the isomer, 1-



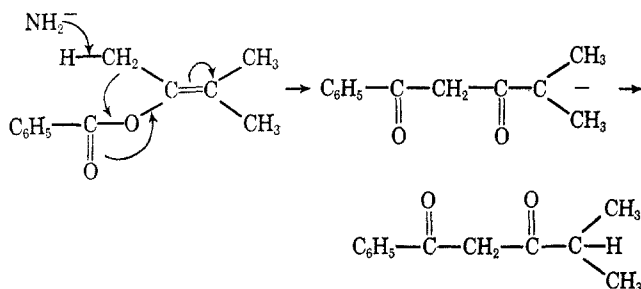
(12) These data will be reported in a later paper.

(13) G. T. Morgan, H. D. K. Drew, and C. R. Porter, *Ber.*, 58, 333 (1952).

(14) G. T. Morgan and R. W. Thomason, *J. Chem. Soc.*, 754 (1924).

(15) See Table IV, footnote g.

phenyl-4-methyl-1,3-pentanedione. This was confirmed by mixture melting point of its copper chelate with an authentic sample. Similarly, the rearrangement of 2-pentanone enol benzoate with sodium amide gave 1-phenyl-1,3-hexanedione and not 1-phenyl-2-ethyl-1,3-butanedione. A possible intramolecular mechanism which could account for the observed product would be an α,γ shift, through the intermediate formation of a four-atom ring, involving the carbon atom α to the double bond.



Experimental Section¹⁶

Materials.—Ketones were obtained commercially, redistilled before use, and checked for purity by gas chromatographic analysis and by comparison of refractive indices with literature values. Acid chlorides and acid anhydrides were distilled. Sodium amide (purity 90%) under mineral oil was washed twice under nitrogen with anhydrous ether and used without further purification. *p*-Toluenesulfonic acid was used as received.

4,4-Dimethyl-2-pentanone^{17,18} was synthesized in 45% yield by the pyrolysis of ethyl *t*-butylacetoacetate at 540–550° in a flow reactor under nitrogen. The impure product was diluted with ether, washed with sodium bicarbonate solution and water, then dried over anhydrous magnesium sulfate. Fractional distillation of the pyrolysate through a 30-cm Vigreux column gave pure 4,4-dimethyl-2-pentanone, bp 128–130° (755 mm), n_D^{20} 1.4105 [lit.¹⁹ bp 123–125° (743 mm), n_D^{20} 1.4038].

Base-Catalyzed Acylation of Ketones.—A typical base-catalyzed acylation using benzoyl chloride was carried out as follows. A solution of 2.90 g (0.05 mole) of acetone in 10 ml of anhydrous ether was added to a mixture of 2.17 g (0.05 mole) of sodium amide in 10 ml of anhydrous ether. When the initial exotherm had ceased, the reaction mixture was cooled to room temperature and added dropwise to a solution of 14.0 g (0.1 mole) of benzoyl chloride in 20 ml of anhydrous ether. The reaction mixture was stirred by a stream of nitrogen for 1 hr, then the excess ether was removed under reduced pressure. The residue was slurried into iced water, and the oily layer was separated, washed, and dried over anhydrous magnesium sulfate. The reaction mixture was analyzed directly by gas chromatography using measured amounts of toluene (0.5–1.0 g) as internal standard to determine the ratio of O-acylation product (enol ester) to C-acylation product (1,3-diketone). Appreciable solubility of several aliphatic and aromatic 1,3-diketones was noted in the saturated sodium bicarbonate solution used initially

to remove traces of acid and excess acylating agent. Separation of aromatic 1,3-diketones as their copper chelates was unsuccessful because of coprecipitation of cupric benzoate. Gas chromatographic analysis of the reaction mixture, either with an initial fractional distillation to remove acylating agent or without any treatment except washing, was most accurate despite the sensitivity of some enol esters to acid hydrolysis.

Similar acylations were carried out using acetyl chloride and acetic anhydride.

The effects of mode of addition of reactants and the reactant ratios on the distribution of products obtained with various ketones are summarized in Table I. The 1,3-diketones were characterized by their coloration of ethanolic ferric chloride, by their copper chelates, and by mixture melting points with authentic samples where possible (see Table IV).

Acid-Catalyzed Acylation of Ketones.—A typical acid-catalyzed acylation using acetyl chloride was carried out as follows. A mixture of 72 g (1 mole) of 2-butanone, 78.5 g (1 mole) of acetyl chloride, and 0.1 g of *p*-toluenesulfonic acid was refluxed until hydrogen chloride evolution ceased (about 60 hr). The reaction mixture was cooled and washed with saturated sodium bicarbonate solution. Ether extracts of this mixture were washed with water, dried over magnesium sulfate, then fractionated to give 15.4 g (15%) of 2-butanone enol acetate, bp 48–50° (ca. 5 mm), n_D^{20} 1.4470.

Anal. Calcd for $C_6H_{10}O_2$: C, 63.15; H, 8.85. Found: C, 63.3; H, 9.01.

Similar acylations were carried out using benzoyl chloride, and the results are summarized in Table II.

The enol benzoate of 2-propanone was prepared as follows. Benzoyl chloride (70 g, 0.5 mole) was added slowly to 2-propanone enol acetate (100 g, 1 mole) with stirring. Sulfuric acid (1.5 ml, specific gravity 1.84) was then added, and the reaction mixture was refluxed for 12 hr. The cooled mixture was then neutralized with sodium acetate, filtered, then fractionated through a 12-in. spiral column to yield 7.5 g (46%) of slightly impure 2-propanone enol benzoate, bp 100–103° (5 mm).

The purified enol esters were colorless liquids which instantly decolorized 10% bromine-carbon tetrachloride solution. The distribution of possible structural isomers was estimated by gas chromatographic analysis. Pure isomer samples of enol esters were separated by gas chromatography and characterized by their nmr and infrared spectra. Stereochemical assignments for nmr spectra were based on published data for similar types of esters.^{11,20–22} The data will be reported in a later paper.

Rearrangement of Enol Esters to 1,3-Diketones by Sodium Amide.—1,3-Diketones were obtained in good yield by the rearrangement of certain enol benzoate esters in sodium amide suspensions in anhydrous ether. A typical experiment is as follows. A solution of 14 g (0.07 mole) of 4-methyl-2-pentanone enol benzoate in 25 ml of anhydrous ether was poured into a cooled (0°) and stirred suspension of 3.0 g (0.07 mole) of sodium amide in 45 ml of ether. The mixture was refluxed overnight and poured onto ice. Ether extracts, neutralized and dried as previously described, were distilled through a 25-cm Vigreux column to give 11.7 g (84%) 1-phenyl-5-methyl-1,3-hexanedione, bp 98–101° (0.5 mm).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.45; H, 7.90. Found: C, 76.3; H, 7.94.

The compound formed a red enol coloration with ferric ion, and was quantitatively converted to its green copper chelate, mp 102° (no depression in a mixture melting point with an authentic sample).

In a similar manner, 1-phenyl-4-methyl-1,3-pentanedione was obtained in 77% yield from the rearrangement of 3-methyl-2-butanone enol benzoate, and 1-phenyl-1,3-hexanedione in 82% yield from 2-pentanone enol benzoate. No 1,3-diketone was isolated from the treatment of 3-pentanone enol benzoate.

(16) Melting points were measured with a Fisher-Johns apparatus and are corrected; boiling points are uncorrected. Infrared spectra were determined using Perkin-Elmer Model 221 recording spectrophotometers fitted with sodium chloride prisms. Nmr spectra, measured at 60 Mc, were obtained on a Varian HR-60 nmr spectrometer by Mr. W. Anderson of Stanford Research Institute. Gas chromatographic analyses were carried out on an F & M Model 720 gas chromatograph or Wilkens Aerograph Model 200 using a variety of columns and helium as carrier gas. Microanalyses were carried out by Dr. E. Meier, Stanford University Chemistry Department Microanalytical Laboratories.

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