permit coagulation, and was then filtered off and washed with water. Evacuation at 1 mm over potassium hydroxide for 24 hr afforded 5.6 g (84%) of the dry salt.

Dry distillation of the salt was carried out in a 25-ml distillation flask whose side arm was connected to two ice–water traps in series. A plug of glass wool was placed in the neck of the flask to prevent solid from leaving the bulb. The pressure in the system was slowly reduced to ca. 1 mm, and the flask was heated with a Wood's metal bath. Decomposition began at about 370°, and the bath was maintained between 400 and 500° for 1 hr. There was obtained 1.4 g of brownish liquid which was subjected to vpc collection (12-ft Apiezon L, 170°) to give 200 mg (7%) of the silacyclooctanone as a clear liquid. The ketone (n^{26}D 1.4754) was the only major component of the mixture produced in the pyrolysis. It exhibited a carbonyl absorption (neat liquid, Perkin-Elmer Model 421 spectrophotometer) at 1701 cm^{-1}.

Anal. Calcd for $C_9H_{18}OSi$: C, 63.47; H, 10.65. Found: C, 63.39; H, 10.57.

The 2,4-dinitrophenylhydrazone prepared from this ketone melted at 134.5–135.0° (softened at 132°).

Anal. Calcd for $C_{15}H_{22}N_4OSi$: C, 51.41; H, 6.33; N, 15.99. Found: C, 51.59; H, 6.30; N, 16.02.

1,1-Dimethyl-6-hydroxysila-5-cyclononanone (16) and 1,1-Dimethylsila-5-cyclononanol (17).—A 200-ml Morton flask was equipped as in the preparation of acyloin **7**, and the same preliminary steps were observed. The charge to the flask was 120 ml of toluene and 6.0 g (0.26 g-atom) of sodium. Addition of 6.8 g (0.026 mole) of dimethyldi(3-carbomethoxypropyl)silane in 30 ml of toluene was carried out over 7.5 hr. During this time sodium began to adhere to the walls of the flask and three further portions (ca. 3 g each) were intermittently introduced.

The reaction was stirred for 45 min after the last of the diester was added, and then hydrolyzed by adding 25 ml of methanol followed by 60 ml of 1:1 sulfuric acid–water. Sodium was still present in the reaction mixture when the latter was added, and evidently resulted in partial reduction of the acyloin (*vide infra*). Work-up as usual gave 2.4 g (47%) of material which boiled at 79–94° (0.4 mm), and was shown by vpc analysis (4-ft Apiezon L, 160°) to be a mixture of two compounds in an approximate ratio of 2:3 (in order of elution). The first of these was identified as 1,1-dimethylsila-5-cyclononanol.

Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90. Found: C, 65.15; H, 12.05.

The 3,5-dinitrobenzoate prepared from this alcohol melted at 62.0–63.0°.

Anal. Calcd for $C_{17}H_{24}N_2O_6Si$: C, 53.67; H, 6.36; N, 7.37. Found: C, 53.55; H, 6.44; N, 7.29.

The major product of the cyclization reaction was found to be unstable to vpc. When the material was subjected to gas chromatography on a 4-ft stainless steel Apiezon L column in conjunction with a glass-lined injection port, decomposition was minimized. A sample collected under these conditions afforded a correct analysis for 1,1-dimethyl-6-hydroxysila-5-cyclononanone.

Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 60.11; H, 10.09.

The semicarbazone of this acyloin melted at 171.5–172.0°.

Anal. Calcd for $C_{11}H_{23}N_3O_2Si$: C, 51.33; H, 9.01; N, 16.33. Found: C, 51.49; H, 9.21; N, 16.20.

Lactone Trimer of Dimethylketene

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A new trimer of dimethylketene, 5-hydroxy-2,2,4,4,6-pentamethyl-3-oxo-5-heptenoic acid δ-lactone (1), is reported. The mechanism of its formation is discussed, and new proposals are set forth to rationalize more completely the observed base-catalyzed reactions of dimers of dimethylketene.

Both β-lactone and cyclobutane dimers of ketene,[1] alkylketenes,[2] and dialkylketenes[3,4] have been prepared. Various trimers, tetramers, and polymers of these ketenes have also been prepared. A stable trimer of dimethylketene, 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetrione (2), is formed by base-catalyzed reactions of dimethylketene, its dimers, or its polymers.[5,6] The present paper concerns the formation of a less stable trimer of dimethylketene, 5-hydroxy-2,2,4,4,6-pentamethyl-3-oxo-5-heptenoic acid δ-lactone (1) by base-catalyzed disproportionation of the β-lactone dimer of dimethylketene, 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (3).

In the absence of labile hydrogen atoms, 3 reacts with strong base such as a sodium alkoxide to form an enolate anion.[7] With less than equivalent amounts of

base, other products are formed. Although many products may be postulated, for simplicity the discussion will be limited to those four that are shown below.
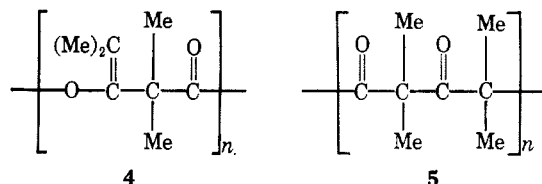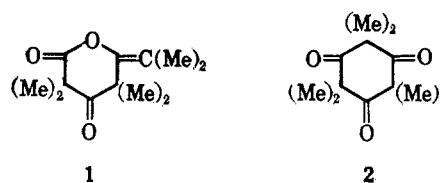
Compounds **1**, **2**, and **4** have been found. Polymer conceivably is formed from **3** by a simple ring opening, like that with β-propiolactone, except that propagation is through the enolate anion rather than the carboxylate anion. Reaction at the oxygen atom of the enolate

(1) N. T. M. Wilsmore and F. Chick, *J. Chem. Soc.*, **97**, 1978 (1910); C. D. Hurd and J. W. Williams, *J. Am. Chem. Soc.*, **58**, 962 (1936); A. B. Boese, *Ind. Eng. Chem.*, **32**, 16 (1940); H. H. Wasserman and E. V. Dehmlow, *J. Am. Chem. Soc.*, **84**, 3786 (1962).

(2) R. B. Woodward and Gilbert Small, Jr., *ibid.*, **72**, 1297 (1950); J. R. Johnson and V. J. Shiner, Jr., *ibid.*, **75**, 1350 (1953).

(3) E. Wedekind and W. Weisswange, *Ber.*, **39**, 1631 (1906).

(4) R. H. Hasek, R. D. Clark, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **27**, 60 (1962).

(5) R. D. Clark (to Eastman Kodak Co.), U. S. Patent 3,173,954 (March 16, 1965); R. G. Nations (to Eastman Kodak Co.), U. S. Patent 3,091,642 (May 28, 1963).

(6) G. F. Pregaglia and M. Binaghi, *J. Org. Chem.*, **28**, 1152 (1963).

(7) R. H. Hasek, R. D. Clark, E. U. Elam, and R. G. Nations, *ibid.*, **27**, 3106 (1962).

anion[8] produces polyester **4**. Reaction at the carbon atom would be expected to produce polyketone **5**. Such a polyketone (or oligomer) also would be expected to degrade from the active end to trimer **1** or **2**, depending on the site of reaction. Furthermore, cleavage of the polyketone **5** by strong base conceivably could begin such a degradation (eq 1).

(1)
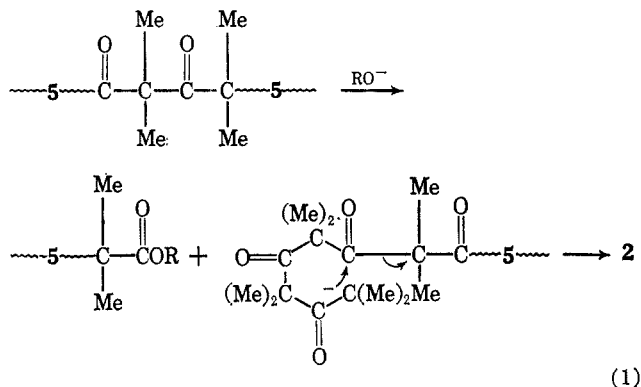
The cleavage and degradation of **5** can indeed occur. Polymer **5**, prepared by the acid-catalyzed polymerization of dimethylketene[9] is *rapidly* degraded to **2** at 190° with sodium methoxide without prior pyrolysis to oligomers, contrary to the report of Pregaglia and Binaghi.[6] Nevertheless, polyketone **5** has not been found in the base-catalyzed reactions of **3** although the other three products (**1**, **2**, and **4**) have been found. Furthermore, trimer **2** can be formed, without a phase separation, in refluxing toluene in which polymer **5** is insoluble.

The relative amount of each product found in the reactions of **3** depends on the temperature and the nature or strength of the basic catalyst.[5,6] With a strong base such as sodium methoxide and a low temperature (refluxing ether), only polyester **4** is formed, but, with such a base at 100°, trimer **2** is formed in high yield in a strongly exothermic reaction. On the other hand, with a weaker base such as sodium hydroxide, polyester **4** is formed exothermically in refluxing **3** (the polymerization reaction is reversible and **3** may be recovered by distillation at 100 mm).[10] Further heating of the mixture at 200–250° without removal of **3** converts the polyester **4** into a mixture of trimers (**1** and **2**). When butyllithium is used as catalyst under similar conditions, the yield of **1** is maximized. Trimer **1** rearranges exothermically to trimer **2** at about 250° with sodium methoxide.

A tentative interpretation of the base-catalyzed reactions of **3**, which is simpler than that previously given,[7] is that **1** and **4** are intermediates in the production of **2**, and that **5** and its oligomers are not normally involved in the process.

$$\text{dimer } \mathbf{3} \longrightarrow \text{polymer } \mathbf{4} \longrightarrow \text{trimer } \mathbf{1} \longrightarrow \text{trimer } \mathbf{2}$$

The most vigorous conditions give **2**. If the base is weak enough or the temperature low enough, appreciable concentrations of **1** and **4** may build up. In the reaction of **3** with butyllithium as catalyst, the

exothermic reaction mixture becomes very viscous initially by formation of polyester **4**. Upon further heating under reflux it becomes less and less viscous. From this mixture **1** and **2** may be distilled.

The conversion of **4** into **1** conceivably involves an intramolecular reaction (at the carbon atom) of the terminal enolate anion with the double bond adjacent to the ester function. The other trimer resulting from reaction at the oxygen atom of the anion has not been observed (eq 2).

(2)
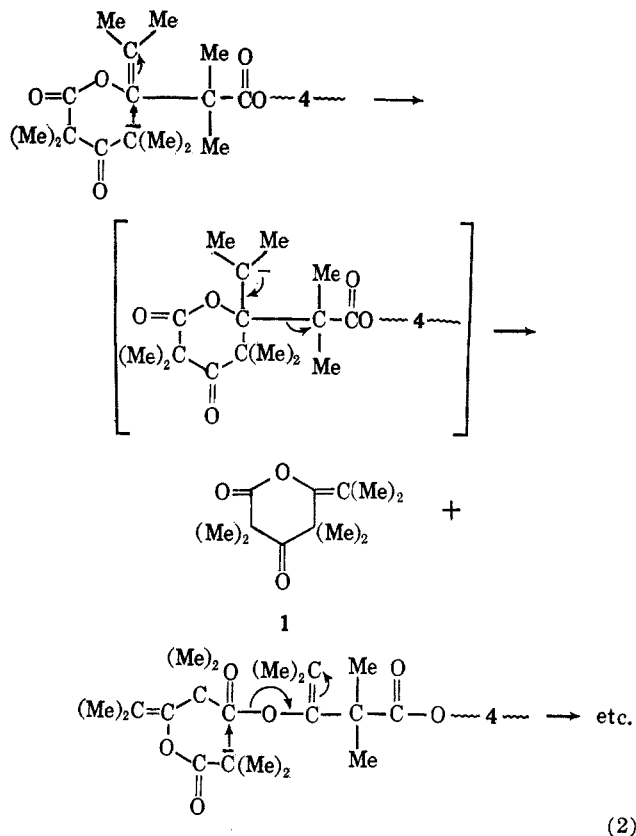
An example of the reaction of an enolate anion with a double bond is the rearrangement of the anion of an allyl ester (eq 3).[11] Danforth observed the nucleophilic

(3)

attack of dimethylamine on the double bond of vinyl acetate with sodium dimethylamide as the catalyst.[12]

Except for attack at the double bond, a similarity exists between the proposed mechanism and the Claisen condensation (eq 4). Cyclization may serve to drive the reaction to completion.


(4)

(8) Although the enolate anion is doubtless a single species by resonance hybridization, its ambient nature has nevertheless been recognized: Y. Yamashita, S. Miura, and M. Nakamura, *Makromol. Chem.*, **68**, 31 (1963).

(9) G. Natta, G. Mazzanti, G. Pregaglia, M. Binaghi, and M. Peraldo, *J. Am. Chem. Soc.*, **82**, 4742 (1960).
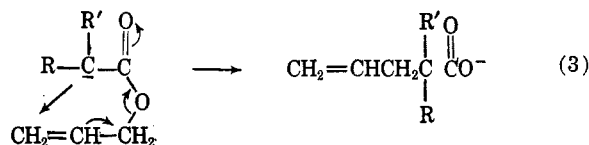
(10) E. U. Elam (to Eastman Kodak Co.), U. S. Patent 3,161,656 (Dec 15, 1964).
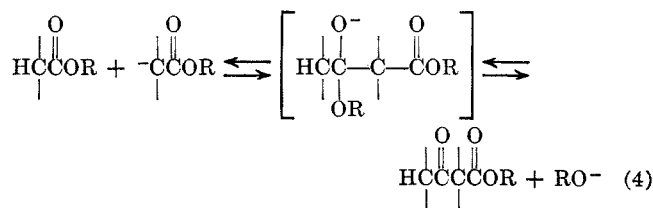
(11) R. T. Arnold and S. Searles, Jr., *J. Am. Chem. Soc.*, **71**, 1150 (1949); R. T. Arnold, W. E. Parham, and R. M. Dodson, *ibid.*, **71**, 2439 (1949).

(12) J. D. Danforth (to Universal Oil Products Co.), U. S. Patent 2,527,709 (March 12, 1950).

SCHEME I

$$^-C(Me)_2\overset{O}{\overset{\|}{C}}C(Me)_2\overset{O}{\overset{\|}{C}}O\!\!-\!\!4\!\sim\;+\;3\;\longrightarrow\;\Big\downarrow A$$

$$\left[\begin{array}{c}(Me)_2\;O\\O\!\!=\!\!C\overset{C}{\diagdown}\overset{\|}{C}\!\!-\!\!\overset{O}{\overset{\|}{C}}(Me)_2CO\!\!-\!\!4\!\sim\\(Me)_2C\diagdown C\!\!-\!\!\bar C(Me)_2\\\overset{\|}{O}\end{array}\right]\longleftrightarrow\left[\begin{array}{c}(Me)_2\;O\\O\!\!=\!\!C\overset{C}{\diagdown}\overset{\|}{C}\!\!-\!\!\overset{O}{\overset{\|}{C}}(Me)_2CO\!\!-\!\!4\!\sim\\(Me)_2C\diagdown C\!\!-\!\!\bar O\\\overset{\|}{C}(Me)_2\end{array}\right]$$
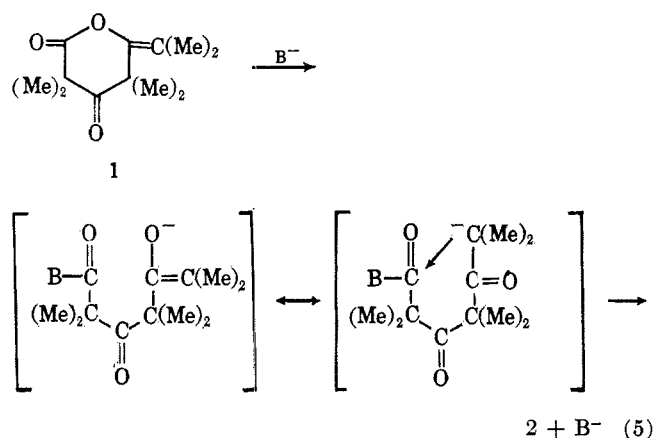
$$\Big\downarrow B \qquad\qquad\qquad\qquad \Big\downarrow C$$

$$2\;+\;1 \qquad\qquad\qquad\qquad 1$$
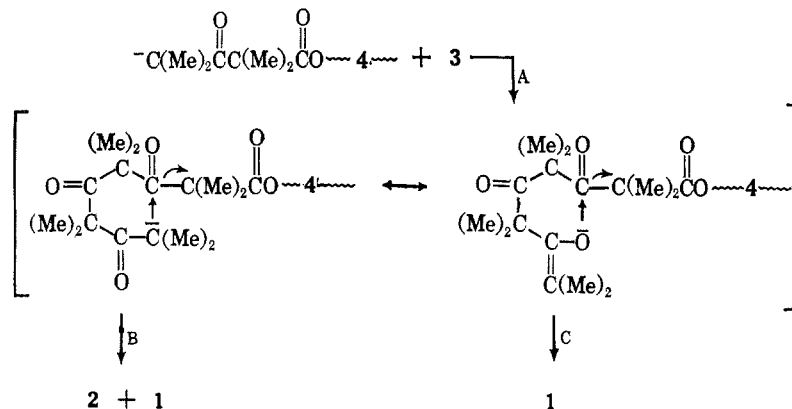
Trimer **2** is formed subsequent to formation of trimer **1** by reaction 5.

$$O\!\!=\!\!\overset{O}{\diagup}\!\!-\!\!C(Me)_2$$
$$(Me)_2\diagdown\;\;(Me)_2$$
$$\overset{\|}{O}$$

1

$$\overset{B^-}{\longrightarrow}$$

$$\left[\begin{array}{c}O\quad O^-\\B\!\!-\!\!\overset{\|}{C}\quad\overset{|}{C}\!\!=\!\!C(Me)_2\\(Me)_2\overset{|}{C}\diagdown C\diagup\overset{|}{C}(Me)_2\\\overset{\|}{O}\end{array}\right]\longleftrightarrow\left[\begin{array}{c}O\;\;^-C(Me)_2\\B\!\!-\!\!\overset{\|}{C}\quad\overset{|}{C}\!\!=\!\!O\\(Me)_2\overset{|}{C}\diagdown C\diagup\overset{|}{C}(Me)_2\\\overset{\|}{O}\end{array}\right]\longrightarrow$$
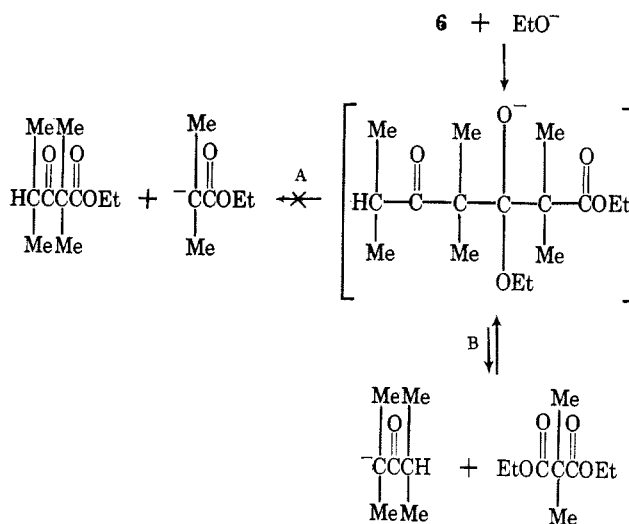
$$2\;+\;B^-\quad(5)$$

The principal objection to the proposed mechanism would appear to be inadequate precedent for attack at the double bond followed by elimination of isobutyrate carbanion. An alternative proposal[7] is that *carbon* acylation of enolate anion is responsible for the six-membered carbon chain of the product. (See Scheme I.)

Presumably, the same intermediate as that from reaction A could be obtained by *carbon* acylation of the anion with polyester **4** followed by anionic degradation to bring the unit of polyketone **5** to the end of the polyester chain. Such a mechanism would require that all of polyester **4** eventually be converted *via* repeated degradation and rebuilding of the polyester containing a "polyketonic defect." No evidence of such a "defect" in the polyester **4** prepared by base-catalyzed polymerization of **3** exists, although its presence has been shown in polyester **4** prepared from dimethylketene.[4,8]

Another disadvantage of this view of formation of **1** is that it requires a *carbon* acylation followed by an *oxygen* acylation–elimination. Oxygen acylations of enolate anions (favored by reactive reagents, *e.g.*, **3**) do not generally occur with weakly acylating agents (*e.g.*, esters), whereas *carbon* acylations do occur. Therefore reactions A and C seem less likely than their alternatives, but the appearance of **1** in major amount is unexplained without invoking path C.

Trimer **1** reacts somewhat like dimer **3** in base-catalyzed reactions. For example, with ethanol and sodium ethoxide, **1** forms ethyl 2,2,4,4,6-pentamethyl-3,5-dioxoheptanoate (**6**). Also its cleavage products,

SCHEME II

$$6\;+\;EtO^-$$
$$\Big\downarrow$$

$$\begin{array}{c}Me\,Me\quad Me\\\overset{|}{H}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OEt\;+\;^-\overset{Me}{\underset{Me}{\overset{O}{\overset{\|}{C}}}}COEt\end{array}\;\overset{A}{\cancel{\longrightarrow}}\;\left[\begin{array}{c}Me\quad Me\;\;\overset{O^-}{|}\;Me\\HC\!\!-\!\!\overset{O}{\overset{\|}{C}}\!\!-\!\!\overset{|}{C}\!\!-\!\!\overset{|}{C}\!\!-\!\!\overset{O}{\overset{\|}{C}}OEt\\\overset{|}{Me}\quad\overset{|}{Me}\;\overset{|}{Me}\\OEt\end{array}\right]$$

$$B\;\Big\Updownarrow$$

$$\begin{array}{c}Me\,Me\\^-\overset{O}{\underset{\overset{|}{Me}\,Me}{\overset{\|}{C}}}CH\;+\;EtO\overset{Me\;\;O}{\underset{Me}{\overset{O}{\overset{\|}{C}}}}COEt\end{array}$$

diisopropyl ketone and diethyl 2,2-dimethylmalonate, are formed. It is interesting that neither of the cleavage products from mode A were found. Apparently cleavage by mode B is highly favored. (See Scheme II.)

The diketo ester **6** has a boiling point different from that of the product of Hudson and Hauser.[13] The basic cleavage is also different from that reported.[13] However, a logical explanation of the data of Hudson and Hauser may be based on the observations of this paper as follows.

Reaction at the oxygen atom of an enolate anion is favored by very reactive acylating or alkylating agents, for example, oxygen acylation of the sodium enolate (**7**) of methyl 2,2,4-trimethyl-3-oxovalerate with dimer **3** to form poly(enol ester) **4**, or oxygen alkylation of **7** with dimethyl sulfate to give methyl 3-methoxy-2,2,4-trimethyl-3-pentenoate. The reaction of the sodium enolate (**8**) of ethyl 2,2,4-trimethyl-3-oxovalerate with isobutyryl chloride or acetyl chloride[13] is such a situation; it is likely that the "diketo esters" of Hudson and Hauser were the isomeric **9** and **10** (eq 6). The interpretation is also in accord with similar exclusive oxygen acylations reported by Yoshida and Yamashita.[14] Furthermore, the methyl esters corresponding to **9** and **10** were prepared by acylation of **7** (prepared from **3** and sodium methoxide). Acylation of **7** has been erroneously reported to give diketo esters.[7] Similarly, acylation of **7** with methyl chloro-

(13) B. E. Hudson and C. R. Hauser, *J. Am. Chem. Soc.*, **61**, 3567 (1939).
(14) K. Yoshida and Y. Yamashita, *Tetrahedron Letters*, 693 (1966).

SCHEME III
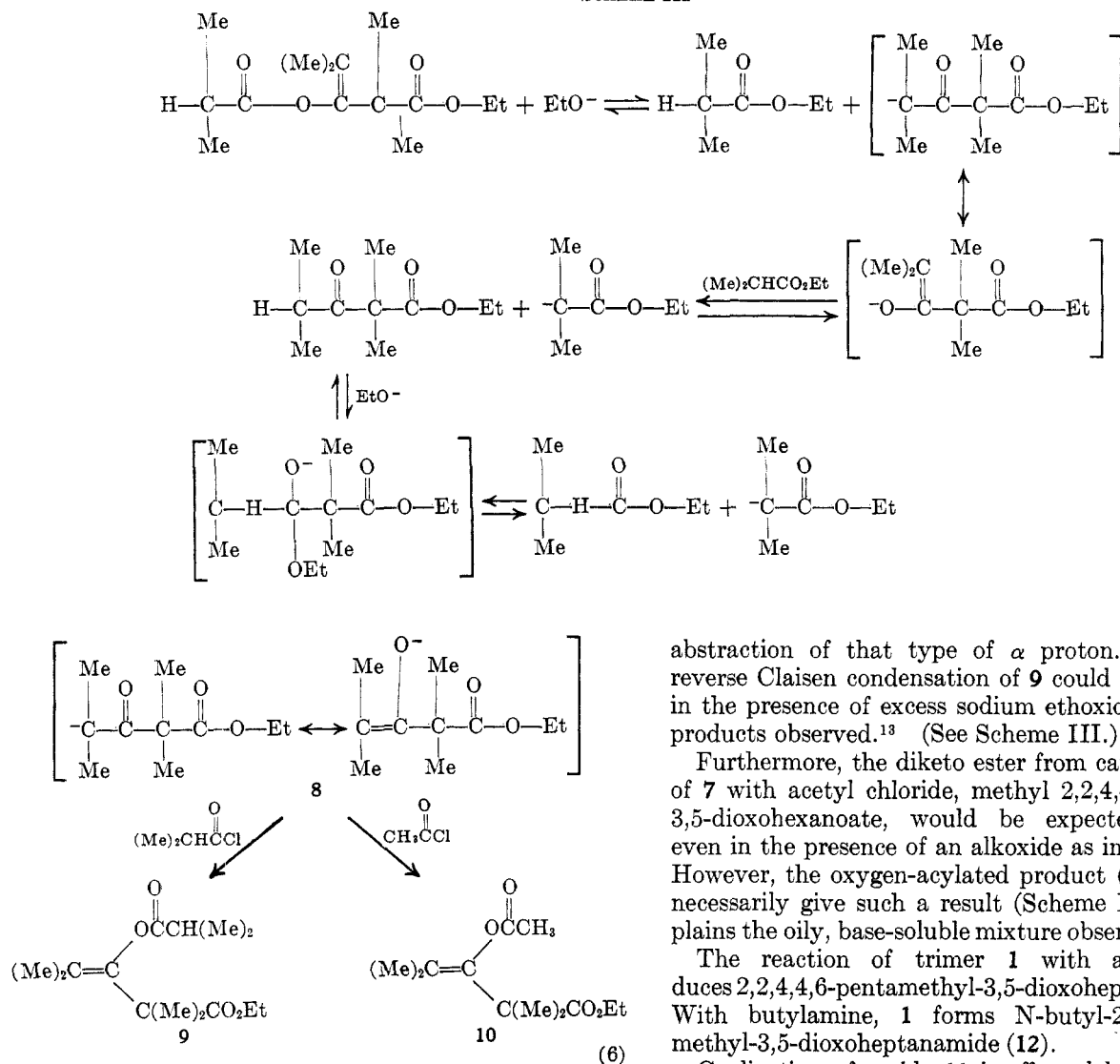
formate gives methyl 3-(methoxycarbonyloxy)-2,2,4-trimethyl-3-pentenoate instead of the reported dimethyl 2,2,4,4-tetramethyl-3-oxoglutarate.[7]

Treatment of 9 with sodium triphenylmethide probably would afford 2 *via* 1, accounting for the product obtained by Hudson and Hauser.[13] (See eq 7.)
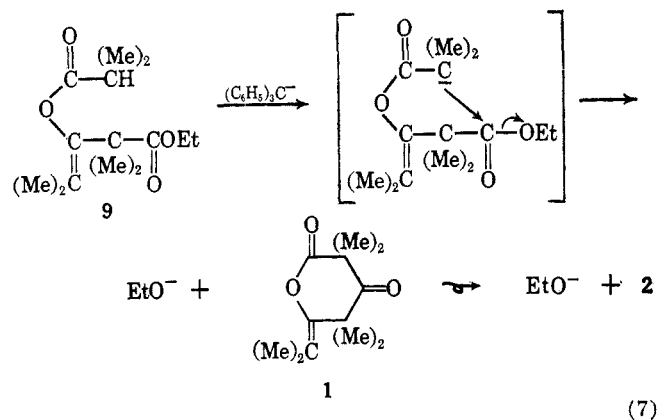
Treatment of 9 with sodium ethoxide[13] would not be expected to cause this reaction to occur, because as reported[15] the alkoxide anion is not basic enough for

abstraction of that type of α proton. However, a reverse Claisen condensation of 9 could logically occur in the presence of excess sodium ethoxide to yield the products observed.[13] (See Scheme III.)

Furthermore, the diketo ester from carbon acylation of 7 with acetyl chloride, methyl 2,2,4,4-tetramethyl-3,5-dioxohexanoate, would be expected to cyclize even in the presence of an alkoxide as indeed it does.[16] However, the oxygen-acylated product (10) would not necessarily give such a result (Scheme IV). This explains the oily, base-soluble mixture observed.[13]

The reaction of trimer 1 with ammonia produces 2,2,4,4,6-pentamethyl-3,5-dioxoheptanamide (11). With butylamine, 1 forms N-butyl-2,2,4,4,6-pentamethyl-3,5-dioxoheptanamide (12).
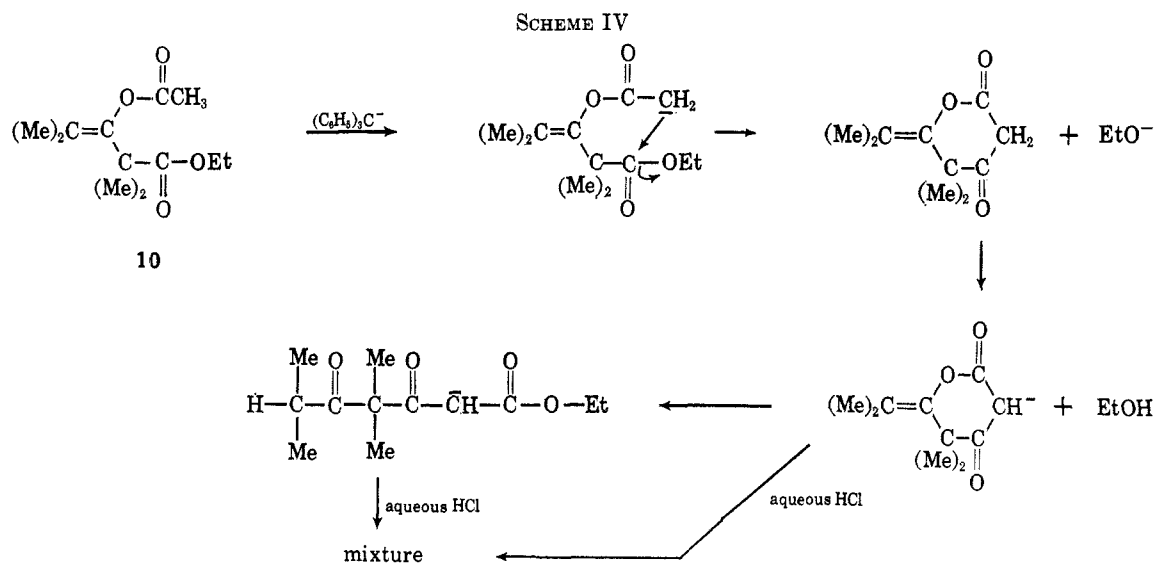
Cyclization of amide 11 is effected by heating, but the product has an exocyclic double bond. The double bond does not migrate into the ring even upon heating the compound to a temperature of 140° (eq 8).
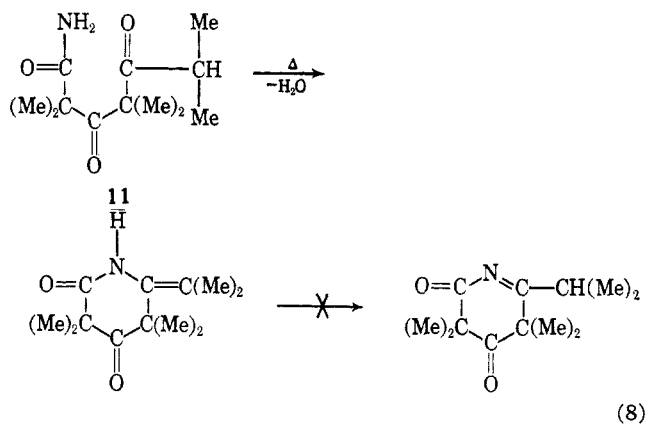
In view of these results, it is surprising that amide 12 will not cyclize even upon prolonged heating at 200°.

It is obvious from the discussion, that the base-catalyzed reactions of dimethylketene, its dimers, its trimers, and its polymers are quite complex. Other

(15) C. R. Hauser and W. B. Renfrow, Jr., *J. Am. Chem. Soc.*, **59**, 1823 (1937); S. M. McElvain, *ibid.*, **51**, 3124 (1929).

(16) B. Murin, W. Riedl, K. H. Risse, and M. Scheublein, *Chem. Ber.*, **92**, 2033 (1959).

SCHEME IV

explanations may be possible; these are presented to clarify formerly anomalous results and to formulate a reasonably consistent picture of the system with the data presently available.

Experimental Section[17]

5-Hydroxy-2,2,4,4,6-pentamethyl-3-oxo-5-heptenoic Acid δ-Lactone (1).—To 210.0 g of 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (3)[4] was added 40 ml of a 15% solution of butyllithium.[18] An exothermic reaction occurred and raised the temperature to 160°. The mixture was then distilled to a head temperature of 180° (pot 250°) over a period of 30 min. The remainder was distilled *in vacuo*, bp 100–120° (8–9 mm), yield 154.8 g (74%).

The product was redistilled through a 1.8 × 45 cm Podbielniak column. Two main fractions were collected: 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetrione (2),[7] bp 115–120° (10 mm), mp 78–80°, yield, 41.1 g (20%); and 5-hydroxy-2,2,4,4,6-pentamethyl-3-oxo-5-heptenoic acid δ-lactone (1), bp 125–126° (10 mm), n^{19}D 1.4800, yield 77.5 g (37%).

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.5; H, 8.6; mol wt, 210. Found: C, 68.5; H, 8.7; mol wt (ebullioscopic in benzene), 203.

Infrared absorption was at 5.68, 5.84, and 6.00 μ. Nmr (neat) showed 1.33 (6 H), 1.42 (6 H), 1.83 (3 H), and 1.92 (3 H).

Rearrangement of Trimer 1 to Trimer 2.—Ten grams of 1 was heated to 250°. To it was added 0.15 g of sodium methoxide. An exothermic reaction occurred; when it had subsided the mixture was immediately cooled to room temperature. The solid was recrystallized from a mixture of 40 ml of methanol and 18 ml of water, washed with two 100-ml portions of water, and air dried, yielding 7.15 g (71%), mp 78–80°. The infrared spectrum was identical with that of an authentic sample of 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetrione.[7]

Polymerization of 3 with Butyllithium.[19]—A mixture of 50 ml of dry cyclohexane and 50 ml of freshly distilled 3 was heated to reflux. To it was added 0.25 ml of a 15% solution of butyllithium in hexane.[18] The mixture was heated under reflux for 2 hr and then allowed to stand for 60 hr at room temperature.

Cyclohexane (150 ml) was added and the solid was filtered off. The solid was washed well with acetone and air dried, yielding 24 g (50%), mp 192–198°, inherent viscosity in phenol tetrachloroethane (60–40), 0.99. The infrared spectrum was identical with that reported for the poly(enol ester) 4.[20]

Degradation of the Polyketone (5) with Sodium Methoxide.—Five grams of 5[9] was mixed with 20 ml of decahydronaphthalene

and the mixture was heated to boiling. The soft polymer was then kneaded with 0.5 g of sodium methoxide in the boiling decahydronaphthalene until all the polymer had dissolved. This required about 10 min. The insoluble material was filtered off and the filtrate was cooled to −20°. The solid which crystallized was filtered off and air dried, yielding 2, 2.8 g (56%), mp 78–80°. The infrared spectrum was identical with that of an authentic sample of 2,2,4,4,6,6-hexamethyl-1,3,5-cyclohexanetrione.[7]

Reaction of 1 with Ethanol.—Sodium (0.9 g) was dissolved in 200 ml of absolute ethanol and the mixture was heated to boiling. To the mixture was gradually added 210.0 g of 1 as fast as boiling from the exothermic reaction would allow. After addition was complete, the mixture was allowed to stand for 30 min and then was poured into ice water. The mixture was made slightly acidic with sulfuric acid and the layers were separated. The organic layer was washed once with aqueous 2% sodium bicarbonate and then dried with anhydrous magnesium sulfate. The drying agent was filtered off and the filtrate was distilled through a 1.8 × 50 cm column packed with protruded stainless steel packing.

Three products were obtained: diisopropyl ketone, 46.2 g (41%), bp 56–57° (69 mm), n^{22}D 1.3976, infrared spectrum identical with that of an authentic sample of diisopropyl ketone;[21] diethyl 2,2-dimethylmalonate, 72.9 g (39%), bp 91–93° (15 mm), n^{20}D 1.4130, infrared spectrum identical with that of an authentic sample of diethyl 2,2-dimethylmalonate;[7] ethyl 2,2,4,4,6-pentamethyl-3,5-dioxoheptanoate (6), 82.0 g (32%), bp 113–114° (3 mm), n^{21}D 1.4472 (boiling point in disagreement with the literature).[13]

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.6; H, 9.4; mol wt, 256. Found: C, 66.0; H, 9.5; mol wt (ebullioscopic in acetone), 256.

Infrared absorption was at 5.75, 5.82, and 5.92 μ. Nmr (50% in carbon tetrachloride) showed 1.01 doublet [gem-(CH₃)₂], 1.27 triplet (CH₃), 1.30 singlet [gem-(CH₃)₂], 1.37 singlet [gem-(CH₃)₂], 3.5 multiplet (H), and 4.12 quartet (OCH₂).

Oxygen Alkylation of the Sodium Enolate (7) of Methyl 2,2,4-Trimethyl-3-oxovalerate.—The enolate (7) was prepared in tetrahydrofuran according to the published procedure.[7] The solvent was not removed but the mixture was stirred and refluxed while 375.0 g of dimethyl sulfate was added over 1.5 hr. The mixture was heated under reflux for 5 hr (accidental loss of the solvent occurred during this period). A mixture of 1 l. of water and 500 ml of 30% ammonium hydroxide was added. The mixture was stirred vigorously and the solid was filtered off. After the layers were separated, the aqueous layer was extracted twice with diethyl ether. The organic extracts were mixed and dried with anhydrous magnesium sulfate which was subsequently filtered off. The solvent was flashed off and the product was distilled, yielding 217.1 g, bp 65–73° (5 mm). Redistillation through a packed column gave three fractions, bp 68.0–68.5° (5 mm), n^{20}D 1.4402–1.4417.

(17) Melting points and boiling points are uncorrected. Chemical shift positions are in ppm with tetramethylsilane as an internal standard.

(18) Foote Mineral Co.

(19) R. D. Clark (to Eastman Kodak Co.), U. S. Patent 3,173,899 (March 16, 1965).

(20) G. Natta, G. Mazzanti, G. Pregaglia, and M. Binaghi, *Makromol. Chem.*, **44–46**, 537 (1961).

(21) "2,2,4-Trimethyl-3-hydroxy-3-pentenoic Acid, β-Lactone," Eastman Chemical Products, Inc., Kingsport, Tenn., 1961, Technical Data Report No. X-129, p 6.

Spectral Data.—Infrared absorption was at 5.75, 5.88, and 6.01 μ. Nmr (neat) showed 1.15 (singlet), 1.30 (singlet), 1.43 (singlet), 1.63 (singlet), 3.45 (singlet), 3.55 (singlet), and 3.62 (singlet). Comparative areas (3.5:1) of peaks at 1.15 [C(CH₃)₃] and at 1.43 and 1.63 ppm [>C=C(CH₃)₂] indicated the presence of about 30% methyl 2,2,4,4-tetramethyl-3-oxovalerate and 70% methyl 3-methoxy-2,2,4-trimethyl-3-pentenoate.

The mixture was then heated for 39 hr in refluxing methanol in which 1.0 g of sodium had been dissolved. During this time the infrared absorption at 5.88 μ disappeared and a new absorption band at 5.83 μ appeared.

The solid was filtered off and the solvent was flashed off. Again solid was removed from the residue and the product was distilled through a Vigreux column, yielding methyl 3-methoxy-2,2,4-trimethyl-3-pentenoate, 42.3 g, bp 68–69° (5 mm), n^{20}D 1.4460.

Anal. Calcd for C₁₀H₁₈O₃: C, 64.5; H, 9.7; mol wt, 186. Found: C, 64.4; H, 9.6; mol wt (ebullioscopic in acetone), 203.

Infrared absorption was at 5.75 and 6.01 μ. Nmr (neat) showed 1.28 singlet (6 H), 1.41 singlet (3 H), 1.60 singlet (3 H), 3.45 singlet (3 H), and 3.57 singlet (3 H).

Oxygen Acylation of 7.—The reaction of 7 with acetyl chloride, cyclohexylcarbonyl chloride, and methyl chloroformate has been reported to give carbon acylation.[7] The products prepared by the published procedure were further analyzed.

The product of 7 and acetyl chloride is methyl 3-acetoxy-2,2,4-trimethyl-3-pentenoate.

Anal. Calcd for C₁₁H₁₈O₄: sapon equiv, 107. Found: sapon equiv, 107.

Infrared absorption was at 5.73, 5.80, and 5.98 μ. Nmr (30% in carbon tetrachloride) showed 1.27 (6 H); 1.49 and 1.55 [>C=C(CH₃)₂], 2.11 (3 H), and 3.65 (3 H).

The product of 7 and cyclohexylcarbonyl chloride is methyl 3-(cyclohexylcarbonyloxy)-2,2,4-trimethyl-3-pentenoate.

Anal. Calcd for C₁₆H₂₆O₄: sapon equiv, 141. Found: sapon equiv, 146.

Infrared absorption was at 5.78, 5.88, and 6.00 μ. Nmr (30% in carbon tetrachloride) showed 1.27 (6 H); 1.48 and 1.56 [>C=C(CH₃)₂], 3.65 (3 H), and broad absorption at 1.2–2.7.

The product of 7 and methyl chloroformate is methyl 3-(methoxycarbonyloxy)-2,2,4-trimethyl-3-pentenoate.

Spectral Data.—Infrared absorption was at 5.71, 5.82, and 5.91 μ. Nmr (30% in carbon tetrachloride) showed 1.32 (6 H), 1.56 (6 H), 3.71 (3 H), and 3.83 (3 H).

This product apparently was *not* identical with that of Murin, *et al.*,[16] because its saponification by an identical procedure did not give 2,2,4,4-tetramethyl-3-oxoglutaric acid but rather carbon dioxide and diisopropyl ketone (35%), identified as its 2,4-dinitrophenylhydrazone, mp 93–95°.

Acylation of 7 with isobutyryl chloride was carried out by the published procedure.[7] The yield of methyl 3-isobutyryloxy-2,2,4-trimethyl-3-pentenoate was 48%, bp 93–96° (2.3 mm).

Spectral Data.—Infrared absorption was at 5.81, 5.92, and 6.00 μ. Nmr (30% in carbon tetrachloride) showed 1.22 doublet and 2.64 septet [CH(CH₃)₂], 1.28 (3 H), 1.30 (3 H), 1.46 and 1.53 [>C=C(CH₃)₂], and 3.64 (3 H).

Reaction of 1 with Ammonia.—A mixture of 20.0 g of 1 and 250 ml of 30% ammonium hydroxide was stirred vigorously for 3 hr. The solid was filtered off, washed with three 100-ml portions of water, and then dried in a forced-air oven at 100°, yielding 2,2,4,4,6-pentamethyl-3,5-dioxoheptanamide (11), 14.6 g (68%), mp 188–190°.

Anal. Calcd for C₁₂H₂₁NO₃: C, 63.4; H, 9.3. Found: C, 63.6; H, 9.3.

Infrared absorption was at 2.83, 3.11, 5.85, and 6.0ʹμ. Nmr (10% in pyridine) showed 1.10 doublet (3 H), 1.25 singlet (3 H), 1.31 doublet (3 H), 1.47 singlet (3 H), 1.52 singlet (3 H), 1.58 singlet (3 H), 2.32 multiplet (1 H), and 7–8 broad general (pyridine).

A 5.0-g sample of 11 was boiled for 5 min in a test tube. The sample was cooled and recrystallized from ethanol; yield of 6-isopropylidene-3,3,5,5-tetramethyl-2,4-piperidinedione was 2.7 g (59%), mp 178–183°.

Anal. Calcd for C₁₂H₁₉NO₂: C, 68.9; H, 9.2. Found: C, 69.4; H, 9.5.

Infrared absorption was at 3.17, 5.83, and 6.05 μ. Nmr (10% in tetrachloroethane) showed 1.29 (6 H), 1.32 (6 H), 1.77 (3 H), 1.86 (3 H), and 7.99 (1 H). The only change in the nmr spectrum on heating to 140° was a very slight shift up field of the peak at 7.99 ppm.

Reaction of 1 with Butylamine.—A mixture of 100.0 g of 1 and 35.0 g of butylamine was heated at 200° for 30 min. The product was distilled; yield of N-butyl-2,2,4,4,6-pentamethyl-3,5-dioxoheptanamide was 93.4 g (69%), bp 143–144° (1 mm).

Anal. Calcd for C₁₆H₂₉NO₃: C, 67.8; H, 10.3; N, 4.9. Found: C, 67.6; H, 10.7; N, 4.8.

Infrared absorption was at 3.00 and 5.8–6.2 μ. Nmr (25% in carbon tetrachloride) showed 1.07 doublet (6 H), 1.37 singlet (6 H), 1.43 singlet (6 H), 3.2 multiplet (3 H), 6.90 singlet (1 H), and 7 H obscured under peaks 1.43 and 1.07.

Preparation of β-Ketoaldehydes by Acylation of Aldehyde Enamines[1]

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The reaction of 1-N-morpholinoisobutene (II) with acetyl chloride gives, after mild hydrolysis, α-acetylisobutyraldehyde. Direct acetylation, rather than cycloaddition of ketene followed by ring cleavage, is proposed as a probable mechanism. Benzoylation of 1-N-morpholinoisobutene (II) and 1-N-morpholinobutene (IX) gives α-benzoylaldehydes.

Acylation of the enamines derived from ketones, particularly cyclic ketones, is a well-known synthetic method for α acylation of ketones.[2] The acylation with acid halides bearing no α-hydrogen atom is straightforward, and the acylated enamines give, after hydrolysis, the α-acyl derivatives of the original ketones.[3] With an acid chloride that has an α-hydro-

gen atom, the enamine will take up hydrogen chloride to form a ketene *in situ*, which in turn adds to the enamine to give an aminocyclobutanone derivative.[4] The aminocyclobutanones derived from cyclic ketone enamines give on hydrolysis the α-acyl ketones gen-

Harmer, *ibid.*, **28**, 379 (1963); (d) R. D. Campbell and J. A. Jung, *ibid.*, **30**, 3711 (1965); (e) M. Mühlstädt and J. Riemer, *Z. Chem.*, **4** (2), 70 (1964).

(4) Cycloaddition of ketenes to the enamines derived from ketones and aldehydes has been reported by various workers; see, for example, (a) G. Opitz, H. Adolph, M. Kleemann, and F. Zimmermann, *Angew. Chem.*, **73**, 654 (1961); (b) G. Opitz, M. Kleemann, and F. Zimmermann, *ibid.*, **74**, 32 (1962); (c) G. Opitz and F. Zimmermann, *Ann.*, **662**, 178 (1963); ref 5–8.

(1) Presented in part at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, Japan, March 1966; Abstract, Section III, p 460.

(2) J. Szmuszkovicz, *Advan. Org. Chem.*, **4**, 1 (1963).

(3) *Cf. inter alia,* (a) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963); (b) G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **29**, 798 (1964); (c) R. D. Campbell and W. L.