trated *in vacuo* and distilled at 80° (bath temperature) (0.2 mm). The distillate, 0.442 g, was collected in a Dry Ice trap. Vapor phase chromatographic analysis of the distillate showed it to be a mixture of which 10% was 2-acetoxycyclohexanone (6.2% yield). Repeating the reaction except for substitution of 2 hr at reflux for the 2 days at room temperature gave a 20.5% yield (lit.[17] 25%).

Registry No.—Thallium triacetate, 2570-63-0; I dinitrophenylhydrazone, 16963-08-9; III dinitrophenylhydrazone, 16963-09-0; IV, 2983-04-2; V, 16963-11-4; VI, 16963-12-5; VII, 16963-13-6; VIII, 16963-14-7; VIII dinitrophenylhydrazone, 16976-43-5; IX, 16963-15-8; IX dinitrophenylhydrazone, 16963-16-9; X, 16963-17-0; X dinitrophenylhydrazone, 16963-18-1; XI, 16963-19-2; XI dinitrophenylhydrazone, 16963-20-5; XII, 14161-45-6; XIII, 16963-22-7; XIV, 14026-24-5; XV, 16963-24-9; XVI, 16963-25-0; XVII, 16963-26-1; XVIII, 16963-27-2; 4-*t*-butylcyclohexanone morpholine enamine, 16963-28-3; cyclohexylmethanol morpholine, enamine, 16963-29-4.

Acknowledgment.—This work was supported by the National Institutes of Health through a predoctoral fellowship to T. J. G., PHS 5 Fl-GM-32,494, and Research Grant PHS 2-R01-GM-09381-05.

Pyrolytic Ring Contraction of 2-Acetoxy-2-methylcyclohexane-1,3-diones[1]

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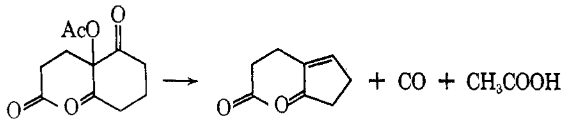
Received February 26, 1968

The pyrolytic ring contraction of 2-acetoxy-2-alkylcyclohexane-1,3-diones to 2-alkyl-Δ^2-cyclopentenones, previously observed only in the case of 2-acetoxy-2-(3-oxobutyl)cyclohexane-1,3-dione (1), has been shown to be a general reaction which proceeds in high yields (60–80%) at temperatures as low as 220°. Acetoxydiones **3** and **4** were prepared in low yield by the reaction of the corresponding 2-methylcyclohexane-1,3-diones with lead tetraacetate. 2-Acetoxy-2-methylcyclopentanone (**5**) was also prepared and was found to pyrolyze to 2-methyl-Δ^2-cyclopentenone under the same conditions as **3**. In ancillary experiments, 2,2-dimethylcycloalkane-1,3-diones **16**, **17**, and **18** were stable at 350°, and 2-acetoxy-2-methylindan-1,3-dione (**19**) evolved only acetic acid at 300–320°.

The remarkably efficient thermal ring contraction observed[3] when 2-acetoxy-2-(3-oxobutyl)cyclohexane-1,3-dione (1) was pyrolyzed at 350° to afford 2-(3-oxobutyl)-Δ^2-cyclopentenone (2) in 70% yield led us to investigate the generality and potential usefulness of this reaction. In this paper the preparation and pyrolytic behavior of two 2-acetoxy-2-alkylcyclohexane-1,3-diones (3 and 4) are described. These substances undergo an analogous loss of carbon monoxide and acetic acid to afford cyclopentenones in good yield at temperatures as low as 220°. The preparation and pyrolysis of 2-acetoxy-2-methylcyclopentanone (5), an intermediate in one of the possible pathways (discussed below) for the conversion of 3 into 2-methyl-Δ^2-cyclopentenone (6), are also described.



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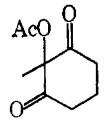

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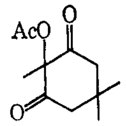

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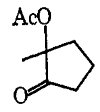

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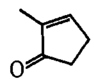

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Preparation of Compounds 3, 4, and 5 for Pyrolysis.—Synthesis of the simplest suitably substituted cyclohexane-1,3-dione, the 2-acetoxy-2-methyl derivative **3**, was first attempted by methylation of 2-acetoxycyclohexane-1,3-dione (**7**).[4] Treatment of **7** in benzene with sodium hydride followed by methyl iodide afforded only a small and variable yield (maximum, 21%) of the desired **3**, mp 103–104°. Accordingly, attention was turned to introduction of the acetoxyl group into the more readily available starting material, 2-methylcyclohexane-1,3-dione (**8**).

Acetoxylation of carbonyl compounds by their reaction with lead tetraacetate has been accomplished in a variety of systems,[5] including β diketones.[6] When **8** was treated with lead tetraacetate in benzene at room temperature for 2 hr, **3** was indeed obtained, but again in a disappointing yield (16%). The predominant product, mp 145–146°, isolated in 27% yield, was assigned structure **9**, mainly on the basis of its elemental analysis and spectral properties, which included ultraviolet absorption consistent with an enol ether of a 1,3-dione and no nmr peaks other than those ascribable to the two methyl groups and the methylene groups of **9**. Mild treatment of the 145–146° substance with aqueous acid afforded **8**, consonant with its structural assignment as **9**.

Compound **9** presumably arises from an unsymmetrical coupling of radical **10**. Symmetrical carbon–

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[1] Portions of this work were presented in the symposium on "The Chemistry of Tall Oil and Turpentine" at the 153rd National Meeting of the American Chemical Society in Miami Beach, Fla., April 1967.

[2] (a) Alfred P. Sloan Foundation Research Fellow. (b) Goodyear Foundation Fellow, 1965–1966.

[3] T. A. Spencer, S. W. Baldwin, and K. K. Schmiegel, *J. Org. Chem.*, **30**, 1294 (1965).

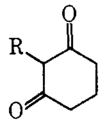
[4] T. A. Spencer, K. K. Schmiegel, and K. L. Williamson, *J. Amer. Chem. Soc.*, **85**, 3785 (1963).

[5] O. Dimroth and R. Schweizer, *Ber.*, **56**, 1375 (1923).

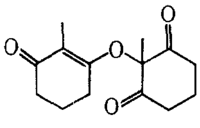
[6] G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 4426 (1955).

carbon bonded dehydro dimers have previously been isolated from the reactions of highly enolic carbonyl compounds with lead tetraacetate.[6] Steric hindrance to carbon–carbon bond formation between two molecules of **10** probably accounts for isolation of the carbon–oxygen bonded **9** in the present case. Several variations in the acetoxylation procedure (*e.g.*, acetic acid as solvent, different temperatures) were tried in unsuccessful attempts to lower the amount of **9** formed relative to **3**. However, an exhaustive study of reaction conditions was not made.

Synthesis of 2-acetoxy-2,5,5-trimethylcyclohexane-1,3-dione (**4**) was accomplished by the analogous reaction of 2,5,5-trimethylcyclohexane-1,3-dione (**11**) with lead tetraacetate. Again the yield of acetoxylation product **4**, mp 146.5–147°, was low (11%), and the predominant product (41%) was enol ether **12**, mp 168–169°, which displayed an unusually detailed nmr spectrum, completely interpretable in terms of structure **12** (see the Experimental Section).



7, R = OAc
8, R = CH_3



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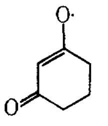

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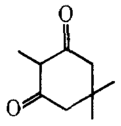

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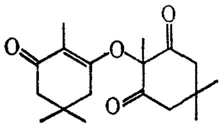

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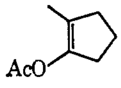

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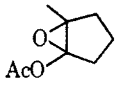

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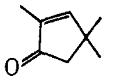

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Preparation of the possible intermediate **5** consisted in epoxidation of the enol acetate **13**[7] derived from 2-methylcyclopentanone. Distillation of the product, presumably **14**, formed in the reaction of **13** with *m*-chloroperbenzoic acid led directly to a good yield of the desired **5**, in another example of the very useful rearrangement of epoxy acetates to 2-acetoxy ketones.[8]

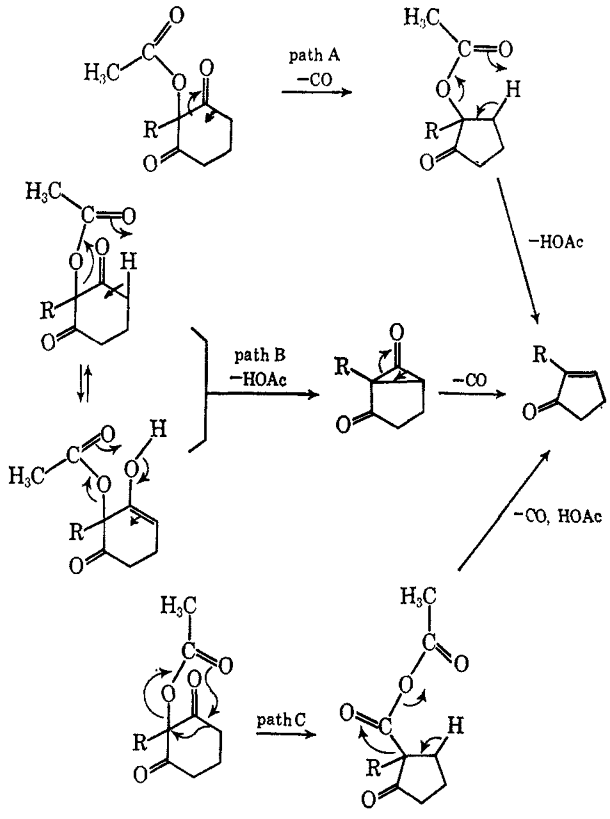
Pyrolyses.—Acetoxydione **3** was first pyrolyzed at 350° in the recycling apparatus[9] which had been used for the pyrolysis of **1**.[3] This was not so convenient in the case of **3**, for conditions could not be found which would permit the essentially complete separation of starting material from product cyclopentenone from acetic acid that had been realized in the pyrolysis of **1**.[3] However, the course of reaction was the same: 2-methyl-Δ^2-cyclopentenone[10] (**6**) was formed in 55% yield (as determined by ultraviolet spectroscopy) and isolated pure in 42% yield from pyrolysis of **3** under these conditions.

As experimentation designed to optimize the yield of **6** progressed, it became evident that the desired thermal ring contraction would occur at much lower temperatures. In fact, the conversion of **3** into **6** can be conveniently conducted in 60–80% yield simply by "refluxing" **3** at *ca.* 220° for 3–4 hr while collecting **6** (which was contaminated with acetic acid) as a distillate.

Analogous results were obtained in the pyrolysis of **4**, which afforded 2,4,4-trimethyl-Δ^2-cyclopentenone (**15**)[11] (73% by ultraviolet spectroscopy), acetic acid, and carbon monoxide upon being heated at 220–240° for 6 hr. Thus this facile thermal ring contraction appears to be general and to proceed in consistently good yields at surprisingly low temperatures. The potential utility of this reaction is limited at present chiefly by the lack of an effective method of preparing the requisite 2-acetoxy-2-alkylcyclohexane-1,3-diones.

The third substance to be pyrolyzed, 2-acetoxy-2-methylcyclopentanone (**5**), is, as noted above, an intermediate in one of the pathways which can be written (see Scheme I) for the conversion of 2-acetoxy-2-alkylcyclohexane-1,3-diones into 2-alkyl-Δ^2-cyclopentenones. The three pathways[12] depicted in Scheme I are distinguished by the order in which acetic acid and carbon monoxide are eliminated; **5** results from initial extrusion of carbon monoxide, as shown in path A.

SCHEME I



When **5** was heated at 220° for 4 hr, the same conditions used for the pyrolysis of **3**, 65% **6** was formed.

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[7] H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

[8] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 120–121.

[9] K. L. Williamson, R. T. Keller, G. S. Fonken, J. Szmuszkovicz, and W. S. Johnson, *J. Org. Chem.*, **27**, 1612 (1962).

[10] O. E. Edwards and M. Lesage, *Can. J. Chem.*, **41**, 1592 (1963).

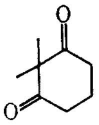
[11] G. F. Hennion and R. B. Davis, *J. Org. Chem.*, **16**, 1289 (1951).

[12] Of the three pathways, C is considered less probable than the others because anhydrides of acetic acid do not usually exhibit this type of behavior on heating. Rather, they are observed to undergo disproportionation to symmetrical anhydrides (C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc., New York, N. Y., 1929, p 575), and one of the principal products (ketene) from pyrolysis of acetic anhydride [M. Szwarc and J. Murawski, *Trans. Faraday Soc.*, **47**, 269 (1951)] has not been detected in the present investigation.

No attempt was made to do accurate rate studies,[13] but monitoring the pyrolyses of **3** and **5** by ultraviolet spectroscopy indicated that **6** is formed at about the same rate in both cases, and that the reaction has gone nearly to completion after 1 hr. On the basis of these experiments, **5** cannot be excluded as an intermediate in the pyrolysis of **3**.

The fact that **5** undergoes thermal elimination of acetic acid apparently[13] at a much lower temperature than 2-acetoxy-2-methylcyclohexanone[14] or 2-acetoxycyclohexanone[9] can be reasonably explained on the basis of the five-membered-ring structure of **5**. The hydrogen and acetoxyl group which enter into the cyclic activated complex for such a *cis* elimination[15] are much more nearly eclipsed in **5** than they are in six-membered-ring systems. Accordingly, less free energy of activation is necessary for pyrolysis of **5** because less distortion is required to reach the transition-state geometry and/or because elimination of the eclipsed substituents relieves nonbonded interactions.

The thermal behavior of some 2,2-dimethylcycloalkane-1,3-diones was briefly examined in a preliminary exploration of the probably unlikely[16] possibility that elimination of carbon monoxide analogous to that postulated in **3** → **5** of path A could be realized in systems in which the product would not react further. 2,2-Dimethylcyclohexane-1,3-dione (**16**), 2,2,5,5-tetramethylcyclohexane-1,3-dione (**17**), and 2,2-dimethylindan-1,3-dione (**18**) were all completely stable at 350° for several hours.



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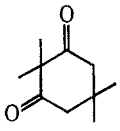

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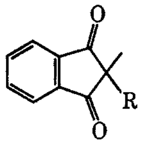
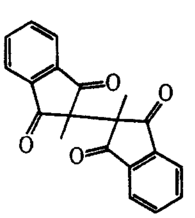


18, R = CH_3
19, R = OAc



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Preparation of a 2-acetoxy-2-alkylcyclohexane-1,3-dione without any hydrogen α to the carbonyl groups, in order to test the importance of a 1,3-elimination mechanism (path B), would be a formidable synthetic task. A readily prepared but obviously imperfect model for such a test, 2-acetoxy-2-methylindan-1,3-dione (**19**), was obtained from the reaction of lead tetraacetate with 2-methylindan-1,3-dione. The desired **19** was accompanied in this case by the carbon-carbon bonded dehydro dimer **20**. Acetoxydione **19** was unaffected by being heated at 220°, but pyrolyzed at 300-320° to afford a black tar and a distillate of acetic acid (61%); however, no carbon monoxide could be detected.

Although the mechanism of the thermal ring contraction of 2-acetoxy-2-alkylcyclohexane-1,3-diones remains uncertain, some clarification can be expected from a study of the analogous pyrolysis of 2-acetoxycycloalkanones to cycloalkenes, which has been observed to occur[9,17] in lower yields at higher temperatures. As Carlson[17] has pointed out, appropriate labeling (deuteration α to the carbonyl group) of the 2-acetoxycycloalkanone to be pyrolyzed should permit a firm experimental distinction between 1,2 elimination (analogous to path A of Scheme I) and 1,3 elimination (analogous to path B) of acetic acid. Unfortunately, such experiments are not applicable to 2-acetoxy-2-alkylcyclohexane-1,3-diones.

Experimental Section[18]

2-Acetoxy-2-methylcyclohexane-1,3-dione (3). A. By Methylation of 2-Acetoxycyclohexane-1,3-dione (7).[19]—To a suspension of 0.150 g (6.25×10^{-3} mol) of sodium hydride powder in dry benzene under a nitrogen atmosphere was added 1.00 g (5.9×10^{-3} mol) of 2-acetoxycyclohexane-1,3-dione (**7**),[4] and the resulting mixture was magnetically stirred overnight. Then 0.5 ml (*ca.* 8×10^{-3} mol) of methyl iodide was added and the mixture was refluxed for 20 hr with a small amount of methyl iodide being added every 3 hr. The mixture was cooled, treated with ice, and extracted with chloroform. The organic layer was dried, filtered, and evaporated to afford an oil which was chromatographed on 30 g of acid-washed alumina to afford, with 1:3 acetone-hexane, 0.232 g (21%) of white solid, mp 103-104°. Recrystallization from ether afforded an analytical sample: mp 103-103.5°; ir (KBr), 5.76 and 5.82 μ; nmr (CCl_4), δ 1.44 (s, 3, $\mathrm{H_3C\text{-}\overset{|}{\underset{|}{C}}\text{-}OAc}$), 2.08 (s, 3, H_3CCOO–), and 1.8-2.8 (m, 6, –CH_2–).

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found C., 58.84; H, 6.52.

B. By Reaction of 2-Methylcyclohexane-1,3-dione (8) with Lead Tetraacetate.—To 7.00 g (0.055 mol) of 2-methylcyclohexane-1,3-dione (**8**) suspended in 500 ml of reagent grade benzene under nitrogen was added 19.5 g (0.044 mol) of lead tetraacetate over a period of 45 min from a flask attached to the reaction vessel by Tygon tubing. The 2-methylcyclohexane-1,3-dione used was commercially prepared material (Aldrich Chemical Co.) which had been recrystallized from 95% ethanol and quickly chromatographed on Florisil to give a dry, odorless, white material, mp 204-208°. The lead tetraacetate used was prepared, purified by recrystallization, and stored according to the procedure given by Fieser.[20] After the mixture was stirred for 2 hr at room temperature, 500 ml of ether was added, and the heterogeneous mixture was transferred to a separatory funnel where it

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[13] It is very difficult to compare meaningfully reaction conditions used for pyrolyses of different substances. It is almost impossible to exclude the possibility that factors such as surface catalysis may be affecting what might be called the "pure" thermal reaction. Furthermore, the influence of various catalytic agents on pyrolyses of acetoxy ketones is not clear. For example, added carbon changes the nature of the products in the pyrolysis of 2-acetoxycyclohexanone, diminishing the yield of Δ^2-cyclohexenone in favor of cyclopentene;[9] on the other hand, carbon was used by H. W. Wanzlich, G. Gollmer, and H. Milz [*Ber.*, **88**, 69 (1955)] in a pyrolysis of 2-acetoxycyclopentanone which afforded a good yield of Δ^2-cyclopentenone at 180-190°. (In view of the present results on the pyrolysis of **5**, the importance of the carbon in Wanzlich's pyrolysis may not have been great.) Potential complications of this kind, although presumably avoidable with extensive painstaking experimentation, were one reason why we did not attempt to compare more precisely the rates of formation of **6** from **5** *vs.* **3**.

[14] E. W. Warnhoff and W. S. Johnson, *J. Amer. Chem. Soc.*, **75**, 494 (1953).

[15] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

[16] Pyrolysis of simple cyclic ketones such as cyclohexanone and 2-methylcyclohexanone produces carbon monoxide only at very high temperatures, and the ring-contracted cycloalkane is not a principal product: C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc., New York, N. Y., 1929, pp 258, 259.

[17] R. G. Carlson and J. H. Bateman, *J. Org. Chem.*, **32**, 1608 (1967). This article provides references to other types of pyrolyses which may occur *via* a 1,3-elimination mechanism, which seems to be these authors' sentimental favorite, as it is ours.

[18] Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were taken in an open capillary and are, like boiling points, uncorrected. Ultraviolet spectra were determined in 95% ethanol solution on either a Bausch and Lomb Spectronic 505 or on a Cary Model 14 spectrophotometer. Infrared spectra were determined on either a Perkin-Elmer Model 21 or Model 137 double-beam recording spectrophotometer. Nuclear magnetic resonance spectra were determined on 10% solutions in carbon tetrachloride or deuteriochloroform containing 5% tetramethylsilane on a Varian Model DA-60 IL instrument. All chemical shifts are in parts per million relative to tetramethylsilane. Vapor phase chromatography was done on a Wilkens Model A 700 chromatograph. Brine refers to saturated sodium chloride solution.

[19] This experiment was performed by Mr. S. W. Baldwin.

[20] L. F. Fieser, "Experiments In Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, pp 325-326.

was washed with 100-ml and 50-ml portions of 1 *N* hydrochloric acid and with two 100-ml portions of brine and was dried over anhydrous sodium sulfate. Evaporation of the filtered benzene layer yielded 8.63 g of wet solid which was chromatographed on 100 g of Florisil to yield two major fractions. The first of these, eluted with 1:1 hexane-ether, gave 1.61 g (16% based on **8**; 21% based on lead tetraacetate) of **3**, mp 94–96°.

The second fraction, eluted with 2:3 hexane–ether, afforded 1.87 g (27%) of the dimeric enol ether **9**, mp 140–144°. Recrystallization from ethanol afforded an analytical sample: mp 145–146°; uv max (95% EtOH), 263 mμ (ε 17,000); ir (KBr), 5.73, 5.82, 6.08, and 6.18 μ; nmr (CCl_4), δ 1.76 and 1.78 (2s, 2 × 3, $H_3C—C=$ and $H_3C—C—O—$), and 1.6–3.1 (m, 12, $—CH_2—$).

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.19; H, 7.39.

Hydrolysis of 9 to 8.—A mixture of 0.481 g (1.92 × 10^{-3} mol) of enol ether **9** and 5 ml of 1 *N* hydrochloric acid was stirred for 8 hr at 50°. The mixture was extracted thoroughly with ether, and the organic layer was dried over sodium sulfate, filtered, and evaporated. The residue was crystallized from ether–ethanol to afford 0.178 g (73%) of **8**, mp 206–208°, which was identified by infrared spectrum.

2-Acetoxy-2,5,5-trimethylcyclohexane-1,3-dione (4).—2,5,5-Trimethylcyclohexane-1,3-dione (**11**) was prepared by methylation of dimedone according to the procedure of Desai.[21] In our hands this preparation typically afforded 41% **11**, 11% 2,2,5,5-tetramethylcyclohexane-1,3-dione [ir (KBr), 5.75 and 5.88 μ], and 15% 3-methoxy-5,5-dimethyl-Δ²-cyclohexenone [ir (film), 6.03 and 6.21 μ]. To a mixture of 10.04 g (0.0653 mol) of **11**, mp 160–163°, and 400 ml of dry benzene was added 30.503 g of lead tetraacetate and the resulting cloudy orange mixture was stirred mechanically for 3 hr at room temperature. The resulting brown mixture was poured into 1 *N* hydrochloric acid and extracted twice with ether. The combined ether layers were washed with brine, dried over magnesium sulfate, filtered, and evaporated to give an oily residue which, upon being allowed to crystallize from *ca.* 60 ml of ether gave first 4.029 g (40%) of dehydrodimeric enol ether **12**, mp 171–172°, after recrystallization from dichloromethane. Recrystallization from ethanol and then from ether afforded an analytical sample of **12**: mp 168–169°; uv max (95% EtOH), 264 mμ (ε 17,900); ir (KBr), 5.71, 5.82, 6.08 and 6.19 μ; nmr ($CDCl_3$), δ 1.01 (s, 9, 3 × H_3C-), 1.17 (s, 3, H_3C-), 1.62 (s, 3, H_3C-C-O-), 1.73 (t, 3, *J* ≅ 2 Hz, $H_3C—C{=}C—CH_2—$), 2.02 (q, 2 *J* ≅ 2 Hz, $—H_2C—C{=}C—CH_3$), 2.22 (s, 2, $—C{=}C—CO—CH_2—C—$), and 2.81 (AB q, 4, J_{app} = 14 Hz, 2 × $—CO—CH_2—C—$).

Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.45; H, 8.40.

The mother liquors from separation of **12** deposited, after standing in the freezer, a second crop of 1.310 g (9%) of the desired **4**. The remaining oil (4.24 g) was combined with 3.64 g of oil remaining from an identical reaction run on 9.99 of **11**, from which 3.28 g (33%) of **12**, and 0.878 g (6%) of **4** had been separated. Chromatography of this 7.88 g of oil on 175 g of Florisil, using hexane–ether mixtures as eluent, afforded 0.908 g more of **4**, for a total yield of 3.10 g (11%) in the two runs. Recrystallization from ether afforded an analytical sample: mp 146.5–147°; ir (KBr), 5.7 (sh) and 5.84 μ; nmr ($CDCl_3$), δ 1.17 (s, 3, $H_3C—C—$), 1.19 (s, 3, $H_3C—C—$), 1.62 (s, 3, $H_3C—C—O—$), 2.16 ($H_3CCOO—$), and 2.60 (AB q, 4, J_{app} = 15 Hz, 2 × $—CH_2—$).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.15; H, 7.72.

2-Acetoxy-2-methylcyclopentanone (5).—2-Methylcyclopentanone, prepared by the reaction of the pyrrolidine enamine of cyclopentanone with methyl iodide,[22] was converted into 1-acetoxy-2-methyl-Δ¹-cyclopentene (**13**) by the action of isopropenyl acetate containing a trace of sulfuric acid.[23] Enol acetate **13**, identical in spectral properties with those reported by House,[7] was thus prepared in 65% yield; vpc analysis on a 5-ft 10% Ucon Polar column at 174° did not reveal the small amount of isomeric enol acetate found by House.[7] To a mixture of 14.51 g of *m*-chloroperbenzoic acid (FMC Corp.) and 300 ml of chloroform at 0° was added 9.40 g (0.067 mol) of enol acetate **13**, bp 47–51° (7 mm). This mixture was maintained at 0° for 2 days and then the precipitated *m*-chlorobenzoic acid, mp 154–155°, was separated by filtration. The chloroform solution was washed with 10% sodium thiosulfate solution, saturated sodium bicarbonate solution until basic, and brine, dried over anhydrous sodium sulfate, and evaporated. The residue was vacuum distilled to afford 7.73 g (74%) of **5**, bp 50–57° (1.2–1.4 mm). Further purification by vacuum distillation yielded the material used in the pyrolysis, which was found already to contain 2% of **6** by uv analysis. By vpc on a 5-ft 10% Ucon Polar column at 168° an analytical sample of **5** was prepared: ir (film), 5.70 and 5.75 μ; nmr ($CDCl_3$), δ 1.32 (s, 3, $H_3C—C—$) and 2.00 (s, 3, $H_3CCOO—$).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.06; H, 7.62.

Pyrolysis of 3 to 2-Methyl-Δ²-cyclopentenone (6).—A 10-ml, pear-shaped flask with a side arm was fitted with a reflux condenser, which was connected to two vapor traps immersed in Dry Ice–acetone baths, and then to a gas exit through mercury. This flask was charged with 3.569 g (0.0194 mol) of **3**, mp 100–101°. The flask was heated slowly in an oil bath as a gentle stream of nitrogen was bubbled into the side arm and through the system. As the oil-bath temperature reached 206° the melted **3** began to bubble and continued to appear to boil throughout the next 3.25 hr, during which time the temperature was raised gradually to 218° and the diminishing, originally colorless, material in the flask slowly turned dark red, while crystals formed in the first trap. (In an earlier experiment, **3** was found to be essentially unchanged upon being heated at 155° for 4 hr.) The following amounts of material were collected: pot residue, 0.491 g; first trap, 1.814 g; second trap, 0.008 g; material washed with ether from condenser, tubing, etc., 0.189 g. Thus a total of 2.502 g or 83% of the theoretical amount, based on loss of 1 equiv of carbon monoxide, was obtained. The trapped material had the strongly characteristic odors of both acetic acid and **6**. Duplicate uv analysis indicated that the first trap contained 77% (by weight) **6** and the washings contained 60% **6**, amounting to 80% of the theoretical yield of **6**.[24] This product was not isolated in this experiment, but it could be readily separated from the contaminating acetic acid by extracting the product in ether solution with 1 *N* sodium hydroxide solution. Distillation of the ether layer afforded pure **6**: bp 155–159°; uv max (95% EtOH), 227 mμ (ε 11,100—an average of three separate determinations of 11,000, 11,200, and 11,000 on **6** purified by vpc on a 5-ft 10% SE-30 column at 147°) [lit.[10] uv max (95% EtOH), 227 mμ (ε 11,220)]; ir (film), 5.87 and 6.08 μ [lit.[10] ir (CS_2) 5.87 and 6.09 μ]; nmr (CCl_4), δ 1.67 (d, 3, *J* = 1.5 Hz, $H_3C—C{=}C—H$), 2.1–2.6 (m, 4, 2 × $—CH_2—$), and 7.23 (m, 1, $H—C{=}C—$).

The 2,4-dinitrophenylhydrazone derivative, mp 218–220° (lit.[25] mp 221–222°), and semicarbazone derivative, mp 218–219° dec (lit.[25] mp 219–220° dec), of **6** were prepared for further proof of its identity.

Pyrolysis of 4 to 2,4,4-Trimethyl-Δ²-cyclopentenone (15).—In an apparatus like that used in the pyrolysis of **3** described above, except that a third trap cooled in Dry Ice–acetone was added, was placed 2.861 g (1.35 × 10^{-2} mol) of **4**, mp 145–146°. The reaction flask was immersed in an oil bath preheated to 218° and heated at 220–240° for 6 hr with a stream of nitrogen passing through the system. The material in the flask gradually changed from colorless to dark red, and cessation of its continuous bubbling after about 6 hr was taken as an indication of completion of

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[21] R. D. Desai, *J. Chem. Soc.*, 1079 (1932).

[22] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

[23] W. G. Dauben, R. A. Micheli, and J. F. Eastham, *ibid.*, **74**, 3852 (1952).

[24] We do not know why the material balance was not better. In earlier experiments (*e.g.*, that reported in ref 3) all the weight except that due to evolved carbon monoxide was recovered. No other gaseous product (such as carbon dioxide) was ever detected. Some product, presumably mostly acetic acid, must have escaped from the system through a leak or past the cold traps.

[25] M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 2955 (1958).

the reaction. The following amounts were isolated: pot residue, 0.511 g; first trap, 0.922 g; second trap, 0.228 g; third trap, 0.15 g; washings from apparatus, 0.328 g. A total of 2.139 or 86% of the theoretical amount, based on loss of 1 equiv of carbon monoxide,[24] was obtained. Ultraviolet analysis of *all* of these materials showed absorption at 229 mμ indicative of the presence of 1.22 g (73%) of **15**.

Isolation of **15** from this pyrolysis was not attempted, but just as in the case of **6** from **3**, the contaminating acetic acid could be removed by extraction with dilute base. A pure sample of **15** was prepared by vpc on a 7-ft 10% Carbowax column at 160° and showed the following spectral data: uv max (95% EtOH), 229 mμ (ε 10,700—an average of three separate determinations of 10,700, 10,600, and 10,900); ir (film), 5.86 and 6.08 μ; nmr (CCl_4), δ 1.19 (s, 6, 2 × $H_3C—\overset{|}{\underset{|}{C}}—$), 1.67 (d, 3, J = 1 Hz, $H_3C—\overset{|}{C}=\overset{|}{C}—H$), 2.13 (s, 2, $—CH_2—$), and 6.93 (q, 1, J = 1 Hz, $H—\overset{|}{C}=\overset{|}{C}—CH_3$).

The 2,4-dinitrophenylhydrazone of **15**, prepared in the usual manner, had mp 215–216° (lit.[11] mp 215–216°).

A sample of the effluent gas from a pyrolysis of **4** was trapped and analyzed by vpc on a 5A molecular sieve column at 80°.[3] A prominent peak, in addition to those due to nitrogen and oxygen, was observed which had a retention time identical with that of an authentic sample of carbon monoxide.

Pyrolysis of 5 to 6.—The apparatus used for the pyrolysis of **3** and **4** was modified by insertion of a Vigreux column and a reflux condenser between the reaction flask and the traps, and by simply blanketing the system with nitrogen rather than entraining vapors from the reaction in a stream of nitrogen. Thus, 6.15 g (3.93 × 10^{-2} mol) of 2-acetoxy-2-methylcyclopentanone (**5**), bp 45–46° (0.7 mm) was essentially refluxed in an oil bath at 220–225° for 4.5 hr. The reaction was monitored by uv spectroscopy on aliquots removed periodically, and was essentially complete after about 1 hr. There was recovered 5.41 g of material in the reaction flask, or 91% of the theoretical amount, taking into account the fact that 0.18 g had been removed for uv analysis.[24] This 5.41 g was 44% **6** by triplicate uv analysis, corresponding to a 63% yield of **6**. Nmr and ir spectra on samples of the product purified by fractional distillation confirmed its identity as **6**.

Attempted Pyrolysis of 2,2-Dimethylcyclohexane-1,3-dione (16).—2,2-Dimethylcyclohexane-1,3-dione was prepared by methylation of **8** with excess potassium carbonate and methyl iodide in refluxing methanol for 6 hr, and was purified by three distillations to give pure **16**: bp 49–51° (0.3 mm); nmr ($CDCl_3$), δ 1.31 (s, 2 × 3, $H_3C—\overset{|}{\underset{|}{C}}—$), *ca*. 2.05 (quintet?, 2, $—CH_2—CH_2—CH_2—$), and 2.71 (t, 2 × 2, $—CH_2—CH_2—CH_2—$). A 10–15-g (0.072 mol) sample of **16** was boiled for 4 hr in an oil bath at 260° through a recycling pyrolysis apparatus[3] at 340°. There was recovered, after cooling and washing all the apparatus, 10.36 g (102%) of a red oil which had an nmr spectrum identical with that of pure **16**.

Attempted Pyrolysis of 2,2,5,5-Tetramethylcyclohexane-1,3-dione (17).—As described above, methylation of dimedone afforded some 2,2,5,5-tetramethylcyclohexane-1,3-dione (**17**), which was purified by recrystallization from hexane to material with mp 92–93° (lit.[21] mp 95°); nmr ($CDCl_3$), δ 0.99 (s, 2 × 3, $H_3C—\overset{|}{\underset{|}{C}}—$), 1.29 [s, 2 × 3, $H_3C—\overset{|}{\underset{|}{C}}—C(=O)—$], and 2.64 (s, 2 × 2, $—CH_2—$). A 4.28-g (0.0255 mol) sample of **17** was boiled for 3 hr in an oil bath at 260° through a recycling pyrolysis apparatus[3] at 360°. There was recovered after cooling and washing all the apparatus 4.10 g (96%) of solid, mp 89–91°, which had an nmr spectrum identical with that of pure **17**.

Attempted Pyrolysis of 2,2-Dimethylindan-1,3-dione (18).—2-Methylindan-1,3-dione, mp 79.5–80.5°, prepared by the method of Koelsch and Byers,[26] was methylated to afford **18**: mp 101–103.5° (lit.[27] mp 106–107°); uv max (95% EtOH), 301 mμ (ε 720), 292 (770), 248 (10,000), and 225 (44,000); ir (KBr), 5.70, 5.84, and 6.27 μ; nmr ($CDCl_3$), δ 1.31 (s, 2 × 3, H_3C–) and 7.9 (m, 4, aromatic H's). A 2.80-g (0.0161 mol) sample of **18** was boiled for 6 hr in an oil bath at 235° through a recycling pyrolysis apparatus[3] at 350°. There was recovered 2.64 (94%) of material, including 0.029 g in the first trap, which had an infrared spectrum identical with that of pure **18**.

Preparation of 2-Acetoxy-2-methylindan-1,3-dione (19).—To a clear yellow solution of 5.06 g (0.032 mol) of 2-methylindan-1,3-dione[26] in 250 ml of benzene was added 15 g of lead tetraacetate. The mixture was stirred overnight, during which time a white precipitate formed, and then was washed well with 1 *N* hydrochloric acid and brine, dried over sodium sulfate, filtered, and evaporated. The residual oil was chromatographed on 100 g of Florisil and there was eluted with 9:1 hexane–ether 0.939 g (13%) of crude **19**. Several recrystallizations from ether afforded an analytical sample: mp 100.5–101°; ir (KBr), 5.68, 5.79 (sh), 5.81, and 6.25 μ; nmr ($CDCl_3$), δ 1.53 (s, 3, $H_3C—\overset{|}{\underset{|}{C}}—O—$), 2.12 (s, 3, $H_3CCOO—$), and 7.9 (m, 4, aromatic H's).

Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 65.96; H, 4.75.

With 1:1 hexane–ether there was eluted a considerably greater amount of solid, mp 178–185°. Several recrystallizations from ether afforded an analytical sample of **20**: mp 204–205°; uv max (95% EtOH), 304 mμ (ε 1400), 293 (1500), 249 (sh) (20,000), and 227 (67,000) [*cf.* uv data on 2,2-dimethylindan-1,3-dione (**18**) cited above]; ir (KBr), 5.71, 5.83, and 6.26 μ; nmr ($CDCl_3$), δ 1.68 (s, 6, 2 × $H_3C—$) and 7.83 (m, 4, aromatic H's).

Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.75; H, 4.71.[28]

No attempt was made to isolate or characterize other products from this reaction.

Pyrolysis of 2-Acetoxy-2-methylindan-1,3-dione (19).—A sample of **19**, mp 94–97°, was heated at 220° for 4 hr under a reflux condenser. An infrared spectrum of the cooled residue was identical with that of the starting material. Next, an apparatus like that described for the 220° pyrolysis of **3** containing 2.745 g of **19**, mp 100.5–101°, was placed in a silicone oil bath at 300°. Over a 2.5-hr period the temperature was raised gradually to 320°, the material in the pot turned dark, and white crystals formed in the Dry Ice–acetone trap. The black tar in the pot weighed 1.879 g; condenser washings weighed 0.141 g; the first trap contained 0.457 g (61%) of >99% pure acetic acid, identified by infrared spectrum and vpc retention time. In a separate experiment, a pyrolysis of **19** was conducted in a closed system designed to trap evolved gas. No significant amount of gas was evolved and vpc analysis of the vapor in the system failed to detect any carbon monoxide.

Registry No.—**3**, 17190-13-5; **4**, 17190-14-6; **5**, 17190-15-7; **6**, 1120-73-6; **8**, 1193-55-1; **9**, 17190-18-0; **12**, 17190-19-1; **13**, 1541-32-8; **15**, 17190-21-5; **16**, 562-13-0; **17**, 702-50-1; **18**, 17190-77-1; **19**, 17190-78-2; **20**, 17190-79-3.

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(26) C. F. Koelsch and D. J. Byers, *J. Amer. Chem. Soc.*, **62**, 560 (1940).

(27) I. N. Nazarov, S. I. Zav'yalov, and M. S. Burmistrova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 197 (1956); *cf. Chem. Abstr.*, **50**, 13762 (1956).

(28) This sample was prepared by Mr. S. Y. Hobbs.