

Thermal and photochemical oxidation of 2-acetylcyclopentanone with atmospheric oxygen

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The major products of thermal (acetone, CaCl_2 excess, reflux) and photochemical (acetone or CCl_4 , room temperature) oxidation of 2-acetylcyclopentanone with atmospheric oxygen are 2-acetyl-2-hydroxycyclopentanone, 2-acetyl-2-hydroxymethylcyclopentanone, 1,1'-diacetyl-1,1'-bicyclopentyl-2,2'-dione, 2-acetoxycyclopentanone, 5,6-dioxoheptanoic acid, glutaric acid, and glutaric anhydride. The formation of 2-acetyl-2-hydroxycyclopentanone is the first example of the direct α -hydroxylation of β -dicarbonyl compound under the conditions described.

Key words: β -diketones, 2-acetylcyclopentanone, oxygen, thermal oxidation, photochemical oxidation.

2-Acetylcyclopentanone (**1**) along with other 2-acylcycloalkanones is used as a polyfunctional synthon for the synthesis of heterocyclic^{1–7} and carbocyclic^{8–12} compounds, complexes with metal ions^{13–16} and boron fluorides,¹⁷ and for other purposes.^{18–21} Diketone **1** was multiply used as a convenient model compound for studying the problems of keto-enol and enol-enol tautomerism in the series of 2-acylcycloalkanones.^{22–25}

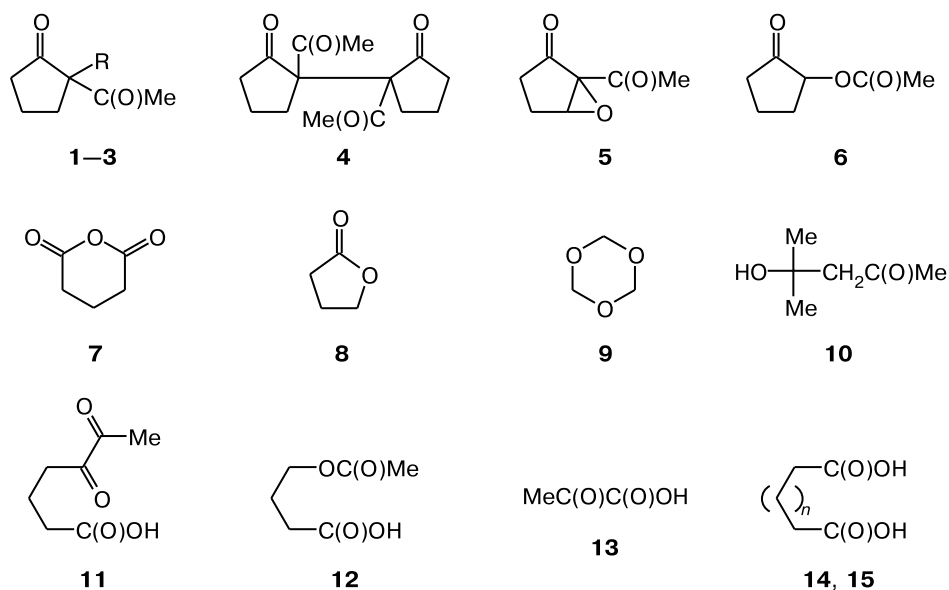
We have earlier found in the synthesis of methyl ethers of the enol form of diketone **1** that the prolonged storage of an ethereal solution of CH_2N_2 and diketone **1** above anhydrous CaCl_2 affords target ethers and considerable amounts of methyl ester of 5,6-dioxoheptanoic acid and products of its further interaction with CH_2N_2 at each carbonyl group. Undoubtedly, the formation of this acid is a result of the oxidation of diketone **1** with molecular oxygen. This fact prompted us to study the processes of interaction of diketone **1** with atmospheric O_2 under various conditions, because this compound is required in organic and analytical chemistry and, hence, its properties should completely be studied.

The oxidation of 2-acylcycloalkanones is considered in many works using as examples 2-acetylcyclohexanone, 2-alkoxycarbonylcyclohexanones, and 2-alkoxycarbonylcyclopentanones or their 6(5)-oxa- and azaheteroanalogs. At the same time, diketone **1** was the subject of the study only in two recent works.^{26,27} The purpose of these works was the development of methods for the α -hydroxylation of 2-acylcycloalkanones, because their α -hydroxylated derivatives are synthetically important products. Oxidants

in these reactions were heavy metal salts ($\text{Pb}(\text{OAc})_4$, $\text{Hg}(\text{OAc})_2$),²⁸ complex reagent oxodiperoxymolybdenum-(pyridine)(hexamethylphosphoramide) (MoOPH),²⁹ oxaziridines,³⁰ dimethyldioxirane,³¹ 2-iodoxybenzoic acid,³² *m*-chloroperoxybenzoic acid,³³ hydrogen peroxide,^{34,35} peroxyacetic acid,³⁶ *p*-chloronitrosobenzene,²⁶ and Oxone.²⁷

Special attention was given to the thermal and photochemical α -hydroxylation of 2-acylcycloalkanones with molecular O_2 .^{37,38} Oxidation with oxygen is usually carried out using the chiral phase-transfer catalysts³⁹ and crown ethers,⁴⁰ anhydrous cesium (CsF or $\text{Cs}(\text{CO}_3)_2$)⁴¹ or cobalt salts (CoCl_2),⁴² hydrates of transition metal salts ($\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (see Ref. 43) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$),^{38,44} and strong bases (Bu^tOK , KH).^{45,46} In the most cases, the oxidation of 1,3-dicarbonyl compounds with O_2 was carried in an oxygen atmosphere, and only some examples for the oxidation in air are described.^{41,47}

The purpose of this work is the detailed study of the oxidative transformations of 2-acetylcyclopentanone (**1**) with air oxygen under different conditions of thermolysis and photolysis. We found that the reflux of a solution of diketone **1** in acetone in the presence of CaCl_2 excess for 30 h resulted in the transformation of ~80% substrate into a complicated mixture of oxidation products. This mixture was preliminarily separated into the neutral and acidic fractions in order to identify the products. Since the acidic properties of the starting 1,3-diketone **1** are not pronounced ($\text{p}K_a$ 7.82 at 20 °C), 1,3-diketone **1** remained among the products of the neutral fraction. 2-Acetyl-2-



R = H (**1**), OH (**2**), CH₂OH (**3**); *n* = 0 (**14**), 1 (**15**)

hydroxycyclopentanone (**2**), 2-acetyl-2-hydroxymethylcyclopentanone (**3**), dimeric 1,3-diketone (**4**), epoxy derivative (**5**), 2-acetoxycyclopentanone (**6**), glutaric anhydride (**7**), γ -butyrolactone (**8**), 1,3,5-trioxane (**9**), and diacetone alcohol (**10**) were identified in the neutral fraction. 5,6-Dioxoheptanoic (**11**), 4-acetoxybutyric (aceburic) (**12**), pyruvic (**13**), succinic (**14**), glutaric (**15**), acetic, and formic acids were identified in the acidic fraction. The weight of the neutral fraction exceeded that of the acidic fraction by ~ 3.5 times.

At room temperature the oxidation occurred slowly, and only $\sim 30\%$ substrate **1** transformed into a mixture of products **2–7**, **14**, **15**, and AcOH after stirring a mixture of diketone **1**, CaCl₂ excess, and anhydrous acetone for 10 days. The yields of the products are listed in Table 1.

Table 1. Conditions of the thermal oxidation of diketone **1*** in acetone and the yields of the products**

<i>T</i> /°C	<i>t</i> /h	Conversion of substrate (%)	Product (yield (%))
57	30	80	2 (38), 3 (5), 4 (11), 5 (2), 6 (2), 7 (7), 8 (2), 9 (1), 11 (13), 12 (2), 13 (1), 14 (1), 15 (7)
25	240	30	2 (31), 3 (7), 4 (6), 5 (10), 6 (8), 7 (2), 14 (1), 15 (2)

* The oxidation of 0.1 *M* solutions of the substrate (0.01 mmol) was carried out in the presence of CaCl₂ excess (0.06 mol).

** Here and in Table 2 the yields of the isolated products based on the reacted substrate are indicated.

In the absence of CaCl₂, reflux of a solution of diketone **1** in anhydrous acetone for 19 h gave no products of substrate oxidation. A similar result was achieved on reflux (30 h) of a mixture of diketone **1** and CaCl₂ excess in anhydrous hexane.

A decrease in the amount of used CaCl₂ to 5 mol.% exerted a negative effect on the course of oxidation of substrate **1** and after reflux for 20 h of a mixture of diketone **1**, CaCl₂, and anhydrous acetone its conversion to the oxidation products did not exceed $\sim 10\%$. The presence of an insignificant amount of water in the reaction mixture inhibited the oxidation of diketone **1**. For example, only $\sim 6\%$ of the substrate transformed into dioxocarboxylic acid **11** on reflux of a mixture of diketone **1** (0.01 mmol), CaCl₂ (0.06 mmol), H₂O (0.001 mmol), and anhydrous acetone for 20 h.

The structures of compounds **2–15** were unambiguously determined from the data of IR spectroscopy, mass spectrometry, and ¹H and ¹³C NMR spectroscopy. In the case of the latter method, different procedures of homo- and heteronuclear spectroscopy were used (COSY 45, DEPT 135, HSQC, and HMBC).

The data of IR and ¹H NMR spectroscopy indicate that the OH group rather than OOH group is in position 2 of 1,3-diketone **2**. It is known that the proton of the hydroperoxide group in the α -position to the CO group appears in the ¹H NMR spectra at δ 8.2–11.5,^{48–52} whereas $\nu_{\text{OO-H}}$ in the IR spectra is observed as an intense band in the range of 3300–3450 cm⁻¹.^{48–51} No signals at δ 8.2–11.5 are observed in the ¹H NMR spectrum (CDCl₃) of compound **2**, and the signal from the proton of the C(2)–OH group appears at δ 3.93 (br.s, 1 H). The IR spectrum (CHCl₃) of diketone **2** exhibits the intense band

$\nu_{\text{O-H}}$ at 3511 cm^{-1} , which in the spectrum obtained in a CCl_4 solution decomposes into two bands with maxima at 3520 and 3476 cm^{-1} . Upon a significant dilution of the solution the band at 3476 cm^{-1} disappears, whereas the band at 3520 cm^{-1} does not change its position and intensity.

The spectral data show that synthesized α -hydroxy-1,3-diketone **2** is completely identical to the α -hydroxylation product of substrate **1**, which has recently been obtained by the oxidation of diketone **1** with *p*-chloronitrosobenzene (75% yield)²⁶ and reagent Oxone (63% yield).²⁷

Based on the data of IR (CHCl_3) and ^1H and ^{13}C spectroscopy (CDCl_3), we can assert that earlier unknown 5,6-dioxoheptanoic acid (**11**) exists in solution only as a chain form. The spectra contain no signals of two theoretically possible ring tautomers, which is well consistent with the properties of the earlier studied δ -oxocarboxylic acids.⁵³

The photooxidation of diketone **1** with air oxygen is faster and more efficient than the thermal one. Direct photochemical reactions were carried out at room temperature in an open conic quartz flask under irradiation of solutions of diketone **1** in different solvents with the full spectrum of a medium-pressure mercury lamp generating UV radiation in the wavelength range 240–320 nm without using photosensitizers.

The most appropriate solvents for the photooxidation of diketone **1** are acetone and CCl_4 , and the solvent nature strongly affected the structure of the products of substrate oxidation and their ratio. Irradiation of a 0.1 *M* solution of diketone **1** in anhydrous acetone at room temperature for 6 h resulted in the complete conversion to a mixture of compounds **2**, **3**, and **5–9**, as well as AcOH and HC(O)OH (Table 2). No formation of dioxocarboxylic acid **11** and dimeric 1,3-diketone **4** was observed. When the irradiation duration decreased to 4 h, the conversion of the substrate was ~80%, and an increase in the irradiation duration to 18 h led to the formation of acetic (~35%), glutaric (~30%), and formic (~10%) acids as the major components in the mixture. The mixture contains also a considerable amount (~10%) of diacetone alcohol **10**.

Irradiation of a 0.1 *M* solution of diketone **1** in anhydrous CCl_4 for 4.5 h resulted in the complete conversion of the substrate to a mixture of compounds **2**, **4–8**, **11**, **14**, and **15** and AcOH (see Table 2). The substrate conversion was ~80% as the irradiation duration decreased to 3 h, while an increase in the irradiation duration to 8 h resulted in the formation of glutaric and acetic acids as the predominant components of the mixture.

No formation of hydroxy diketone **3**, which is one of the major products in the case of acetone, is observed for the photooxidation of diketone **1** in a CCl_4 solution.

In other anhydrous solvents (hexane, benzene, MeCN, or MeOH) the photooxidation of diketone **1** is considerably slower: even upon a prolonged (8 h) irradiation only

Table 2. Conditions of the photochemical oxidation of diketone **1*** and the yields of the products

Solvent	<i>t</i> /h	Conversion of substrate (%)	Product (yield (%))
Me_2CO	6	100	2 (18), 3 (30), 5 (3), 6 (2), 7 (5), 8 (4), 9 (2), 14 (1), 15 (17)
	4	80	2 (36), 3 (22), 5 (2), 6 (1), 7 (3), 8 (3), 9 (1), 14 (1), 15 (13)
	18	100	2 (9), 3 (11), 15 (30)
CCl_4	4.5	100	2 (32), 4 (2), 5 (3), 6 (3), 7 (12), 8 (2), 11 (12), 14 (2), 15 (30)
	3	80	2 (24), 4 (1), 5 (2), 6 (15), 7 (10), 8 (2), 11 (21), 14 (1), 15 (22)
	8	100	2 (20), 5 (2), 6 (2), 7 (8), 11 (9), 15 (43)

* Experiments were carried out at ambient temperature.

a small amount of the substrate transformed into the oxidation products (from ~10% in hexane to ~26% in MeCN). At the same time, in the case of these solvents, the composition of the products was less complicated: the prevailing components were hydroxy diketones **2** and **3** (in MeOH) and dioxocarboxylic acid **11**.

In the presence of a small amount (10 mol.%) of the radical inhibitor, *viz.*, 2,6-di(*tert*-butyl)-4-methylphenol (ionol), the thermal oxidation of diketone **1** with molecular O_2 did not occur even after reflux for 10 h. At the same time, the photooxidation of diketone **1** in the presence of ionol was successful. Under irradiation of a 0.1 *M* solution of diketone **1** and ionol in anhydrous acetone for 7.5 h the yields of compounds **2**, **3**, and **15** were 27, 28, and 31%, respectively, at the complete conversion of the substrate. For the photooxidation of a 0.1 *M* solution of diketone **1** and ionol in anhydrous CCl_4 (3.5 h), the yield of α -hydroxy diketone **2** attained 45% at the complete conversion of the substrate and the yields of acid **11** and ketone **6** were 18 and 17%, respectively.

The results of thermal and photochemical oxidation of diketone **1** with atmospheric O_2 evoke several questions about the mechanism of the process, first of all, formation of the major oxidation products **2–4**, **6**, **7**, **11**, and **15**. It is especially interesting why the oxidation of the substrate at position 2 affords the product with the alcohol function instead of the hydroperoxide function.

Earlier the direct α -hydroxylation of β -dicarbonyl compounds was carried out during thermal oxidation in an oxygen medium using hydrates or anhydrous salts of transition metals. In the case of $\text{Mn(OAc)}_2 \cdot 4\text{H}_2\text{O}$, the formation of 2-hydroxysubstituted 1,3-dicarbonyl com-

pounds was explained by the epoxidation of the enol tautomer of the substrate under the action of the *in situ* formed Mn^V oxo intermediate followed by the rearrangement of generated hydroxyoxirane to the final α -hydroxy ketone.⁴³ When anhydrous $CoCl_2$ was used in a mixture with isopropyl alcohol and MeCN, the formation of 2-hydroxy-1,3-dioxo compounds was attributed to the occurrence of the redox reaction involving O_2 and isopropyl alcohol leading to the formation of water molecule. In the opinion of authors,⁴² the interaction of the latter with the activated intermediates formed from the substrate should afford α -hydroxy ketones. The mechanism based on the *in situ* oxidation of Ce^{III} to Ce^{IV} , the formation of the Ce^{IV} diketone complex in which the intramolecular electron transfer occurs from the ligand to metal, the oxidation of the radical intermediate with the second equivalent of Ce^{IV} , and the interaction of the oxidized intermediate with the water molecule to form the final product was proposed for the direct α -hydroxylation of β -dicarbonyl compounds with molecular O_2 in the presence of cerium salts ($CeCl_3 \cdot 7H_2O$).^{38,44}

Previously, Et_3N as a base and $Pd(10\%)/C$ as a catalyst were used for direct α -hydroxylation of β -dicarbonyl compounds with molecular O_2 in EtOH.³⁷ Unfortunately, the authors gave no comments for the mechanism.

At the same time, the photochemical oxidation of β -dicarbonyl compounds with molecular O_2 resulted, as a rule, in the formation of 2-hydroperoxides,^{49–51,54–57} and for obtaining the target α -hydroxy ketones the reduction of isolated hydroperoxides under the action of Ph_3P , $(EtO)_3P$, $SnCl_2$, or H_2 on $Pd(10\%)/C$ was used.

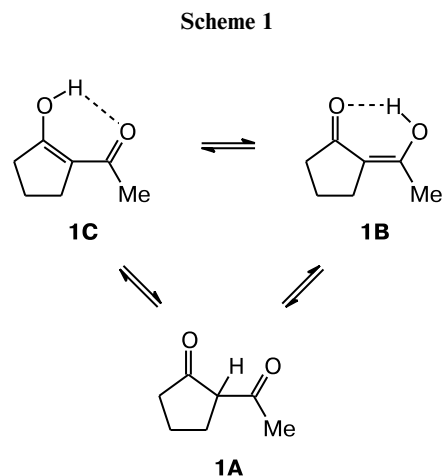
An interesting exception from this rule is the direct photochemical α -hydroxylation of 2-ethoxycarbonylcyclopentanone with molecular O_2 in a $CHCl_3$ solution in the presence of strongly basic Bu_4NF , which gave 2-hydroxy-2-ethoxycarbonylcyclopentanone in a yield of 49%.^{58,59} However, the authors gave no explanation to this fact.

The formation of 2-hydroxy-1,3-dione **2** in our experiments under both the thermal and photochemical oxidation of diketone **1** with molecular O_2 and the preparation of almost the same set of other above mentioned products of its oxidation suggests that they are formed *via* the same routes, but the initial stages of these processes unambiguously differ considerably.

1,3-Diketone **1** in solutions of organic solvents exists as a mixture of diketo form (**1A**) and two enol forms: *exo* (**1B**) and *endo* (**1C**) (Scheme 1).

It has recently²⁵ been shown that the content of diketo form **1A** depends strongly on the solvent polarity and increases with an increase in the polarity.

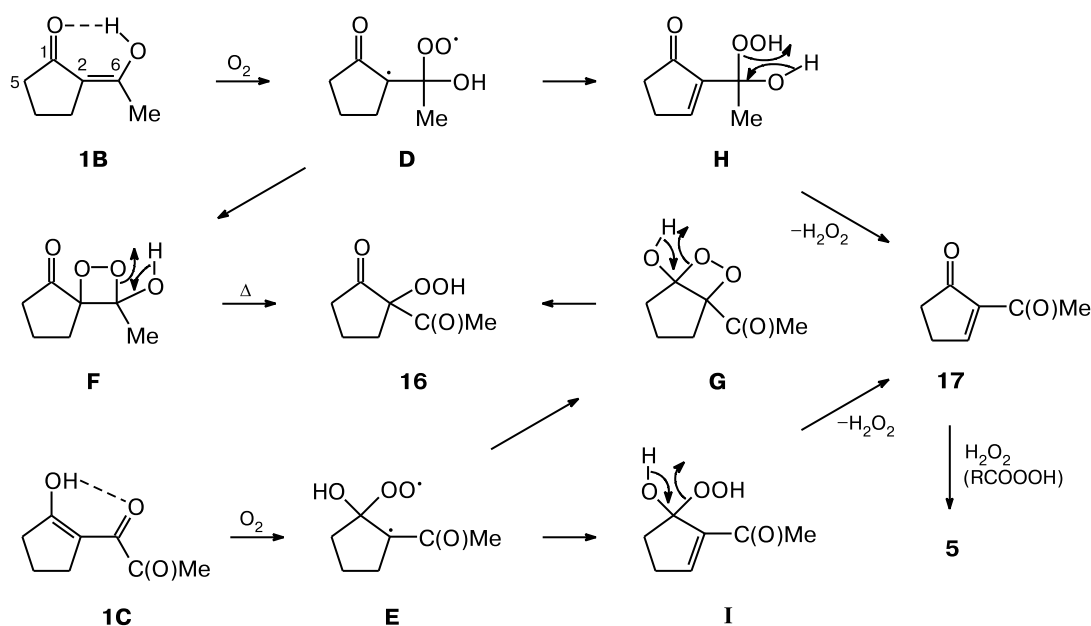
The DFT quantum chemical calculations by the B3LYP/6-31G(d) method shows that the energy of the homolytic cleavage of the π -bond in any enol tautomer **1B** or **1C** does not exceed 30 kcal mol^{-1} , whereas the homo-



lysis of the C(2)—H bond in diketo form **1A** requires $\sim 60 \text{ kcal mol}^{-1}$. Therefore, the enol forms of diketone **1** should be more active in the reactions with molecular O_2 than the diketo form.

The attack of the thermoexcited O_2 molecule to the C(6) atom of enol tautomer **1B** should result in the formation of biradical **D** (Scheme 2), which is transformed, most likely, in dioxetane intermediate **F**. Similarly, the attack of O_2 to the C(1) atom of tautomer **1C** affords biradical **E** and then dioxetane **G**. The thermolysis of each dioxetane gives 2-hydroperoxide **16**. This direction of decay of biradicals **D** and **E** should be predominant, since hydroperoxide **16** can be formed only through this route. As shown in Scheme 3, hydroperoxide **16** should further transform into one of the major oxidation products of the substrate: diketo alcohol **2**. The decay of biradicals **D** and **E** by the H atom abstraction from the C atom in the β -position to the site of attack (the so-called ene reaction)^{49,50,55–57,60} is weak. In this case, α -hydroxy hydroperoxides **H** and **I** that formed should decompose, as shown in Scheme 2, to form the known cross-conjugated 1,3-diketone **17** (synthesized earlier by the oxidation of 2-acetyl-2-methylselenylcyclopentanone with H_2O_2 excess⁶¹) and a hydrogen peroxide molecule. One of the methods for the preparation of H_2O_2 and acetone through the oxidation of isopropyl alcohol with oxygen is based on the property of α -hydroxy hydroperoxides of the **H** and **I** types to decompose easily in the presence of water traces. We failed to isolate diketone **17** in the pure form because of a small content, but its presence among the products of oxidation of diketone **1** is confirmed by the data of the 1H NMR spectra of unseparated mixtures in the case of both thermal and photochemical reactions. Low-intense characteristic signals of compound **17** (δ 2.45 (s, 3 H, COMe), 8.40 (t, 1 H, H(3), $J = 2.7 \text{ Hz}$)) were always observed in these spectra. Its formation is also confirmed by epoxide **5**, which appears due to the further oxidation of enedione **17** under the action of H_2O_2 or, possibly, $RC(O)OOH$.

Scheme 2

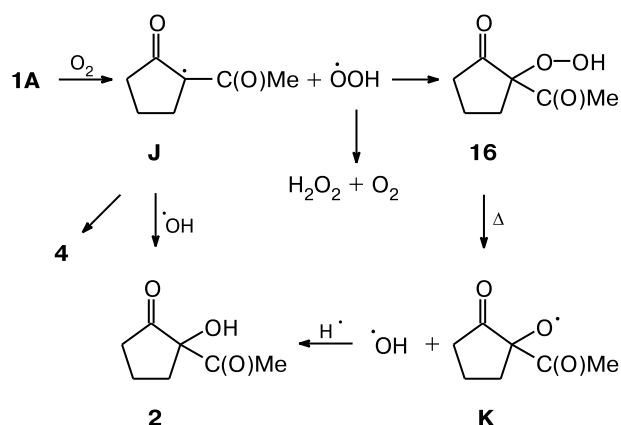


The presence of dimeric 1,3-diketone **4** among the oxidation products of diketone **1** suggests that diketo form **1A** of the substrate also undergoes an attack from the thermoeccited molecule O_2 . Dimer **4** is the product of the bimolecular combination of radicals **J** (see Scheme 3). The interaction of the hydroperoxide radical with radical **J** affords 2-hydroperoxide **16**. The conversion of the latter to diketo alcohol **2** proceeds, probably, through the thermolysis of the O—O bond of hydroperoxide, giving the hydroxyl radical and O-centered radical **K**. The latter is transformed into diketo alcohol **2** by the abstraction of the H atom. In the case of the thermal oxidation of diketone **1**, the donor of the H atom can serve, first of all, a solvent (acetone) molecule. Its participation in radical processes confirms that the reaction mixture contains diacetone alcohol **10**. Another H donor can be a molecule of the initial diketone in the form of **1A**.

As known, salts of variable-valence metals catalyze the thermal cleavage of hydroperoxides of type **16** to form radicals of type **K** (see Scheme 3). In our case, these can be Fe^{II} salts, whose content in the $CaCl_2$ used ranges from 0.0005 to 0.001%. The role of $CaCl_2$, used in a large excess, is reduced, most likely, to the activation of the substrate to oxygen oxidation due to the formation of the Ca^{II} chelate from the starting 1,3-diketone **1**. The salt form of enols **1B** and **1C** should be more active in the oxidation to hydroperoxide **16** than non-enolized 1,3-diketone **1A**. The transformation of the substrate into the form of Ca^{II} chelate is quite possible, since $CaCl_2$ is noticeably dissolved in acetone even at room temperature (0.01 g in 100 mL).

As follows from Schemes 2 and 3, the formation of diketo alcohol **2** from 1,3-diketone **1** under the conditions

Scheme 3

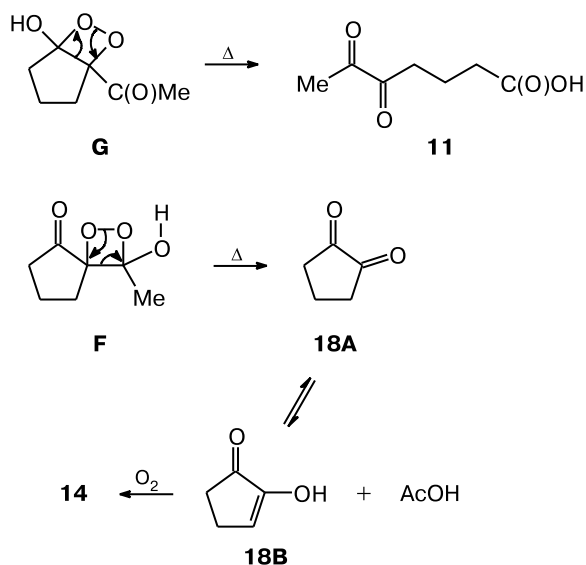


of its thermal oxidation with oxygen should be accompanied by the formation of hydrogen peroxide and, possibly, even some peracids, for example, $MeC(O)OOH$. It is impossible to explain the formation of such isolated oxidation products of diketone **1** as epoxide **5**, acetoxy-cyclopentanone **6**, and acetic acid (**12**) without participation of these oxidants.

This assumption has been advanced first by authors⁵¹ who obtained such products as 2-methylidene-1,3-diones and their epoxy derivatives along with 2-hydroperoxy-2-methyl-1,3-diones by the photochemical oxidation of 1-aryl-2-methyl-1,3-diones. The authors believe that the formation of these products is due to the loss of an H_2O_2 molecule by the intermediate hydroperoxide product.

The second of the major products of diketone **1** oxidation, namely, 5,6-dioxoheptanoic acid (**11**), is formed, probably, due to the thermal ring opening in dioxetane intermediate **G** (Scheme 4).

Scheme 4



The formation of a diketo acid of type **11** has been observed earlier for the thermal oxidation of 2-ethoxycarbonylcyclohexanone with oxygen in the presence of $Mn(OAc)_2 \cdot 4H_2O$ (the yield of 5-ethoxyoxalypentanoic acid is 23%)⁴³ and in the presence of $CeCl_3 \cdot 7H_2O$ (the yield of the acid is 28%).⁴⁴ A similar ring opening in intermediate **F** should afford cyclopentane-1,2-dione (**18**) and

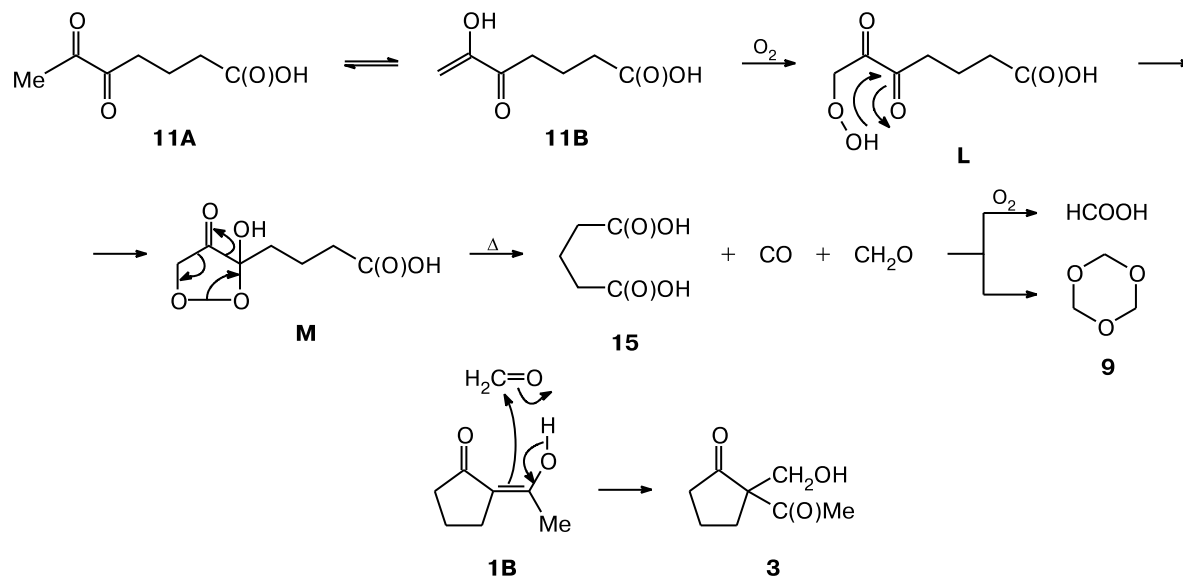
AcOH (see Scheme 4). However, 1,2-diketone **18** was not observed among the reaction products, which is explained, most likely, by the interaction of its enol form **18B** with an O_2 molecule *via* the scheme described earlier⁵⁸ for related 3-methylcyclopentane-1,2-dione. β -Formylpropionic acid formed is further oxidized into succinic acid (**14**).

Thus, the assumption about the formation of dioxetane intermediates **F** and **G** by the thermal oxidation of diketone **1** with molecular O_2 (see Scheme 2) makes it possible to explain reasonably the appearance of diketo alcohol **2** (see Scheme 3) and diketo acid **11** (see Scheme 4) among the predominant reaction products. The possibility of formation of these intermediates by the reactions of 1,3-dicarbonyl compounds with molecular O_2 has been advanced previously.⁶⁰

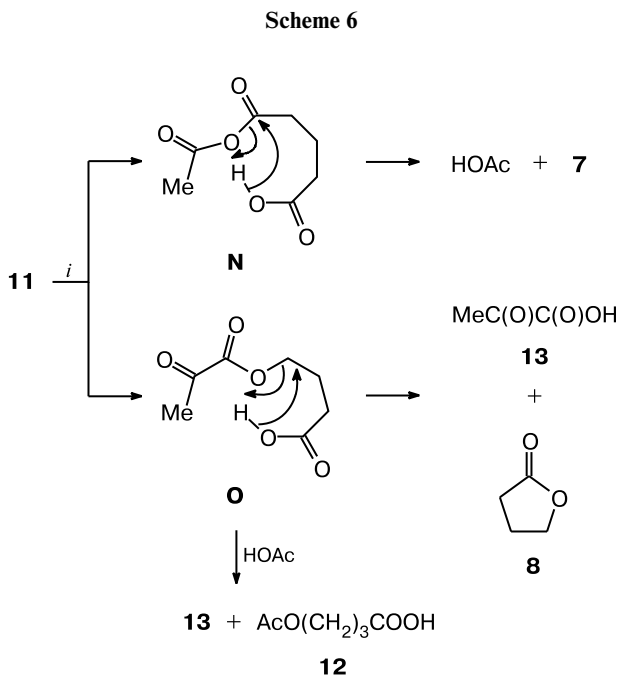
It is most likely that 5,6-dioxoheptanoic acid (**11**) plays the key role in the formation of a considerable number of products of the thermal oxidation of diketone **1** with molecular O_2 . The reaction of enol form **11B** of this acid, being simultaneously 1,2-diketone, with an O_2 molecule should give hydroperoxide **L**, which undergoes ring closure to form peroxide **M** (Scheme 5). The thermolysis of the latter can afford glutaric acid (**15**), formaldehyde, and carbon monoxide. The nucleophilic attack of any of enol forms **1B** or **1C** of diketone **1** to a CH_2O molecule affords 2-hydroxymethyl-substituted 1,3-diketone **3**. Under the reaction conditions, the formaldehyde formed can be partially oxidized to formic acid and partially transformed in cyclic trimer **9**.

Finally, the Baeyer–Villiger oxidation of α -diketone **11** under the action of hydrogen peroxide (or $RC(O)OOH$) present in the reaction medium through intermediate **N** can

Scheme 5



give AcOH and glutaric anhydride (**7**), whereas through intermediate **O** they give a mixture of acid **13** and lactone **8** (Scheme 6). The acetolysis of intermediate **O** can be one of the routes of formation of the known aceburic acid **12**.⁶²



i. H₂O₂ (RC(O)OOH).

The possibility of formation of glutaric anhydride (**7**) from glutaric acid (**15**) under the action of CaCl₂ was excluded by the result of a particular experiment. Reflux of a mixture of glutaric acid (1 mmol) and CaCl₂ excess (6 mmol) in anhydrous acetone for 30 h gave no even trace amounts of anhydride **7**.

If the possibility of occurrence of such a reaction as the Baeyer–Villiger oxidation is excluded from the oxidation of diketone **1** with molecular O₂, it is impossible to understand how such compound as the known 2-acetoxycyclopentanone (**6**) appears among the major reaction products.⁶³

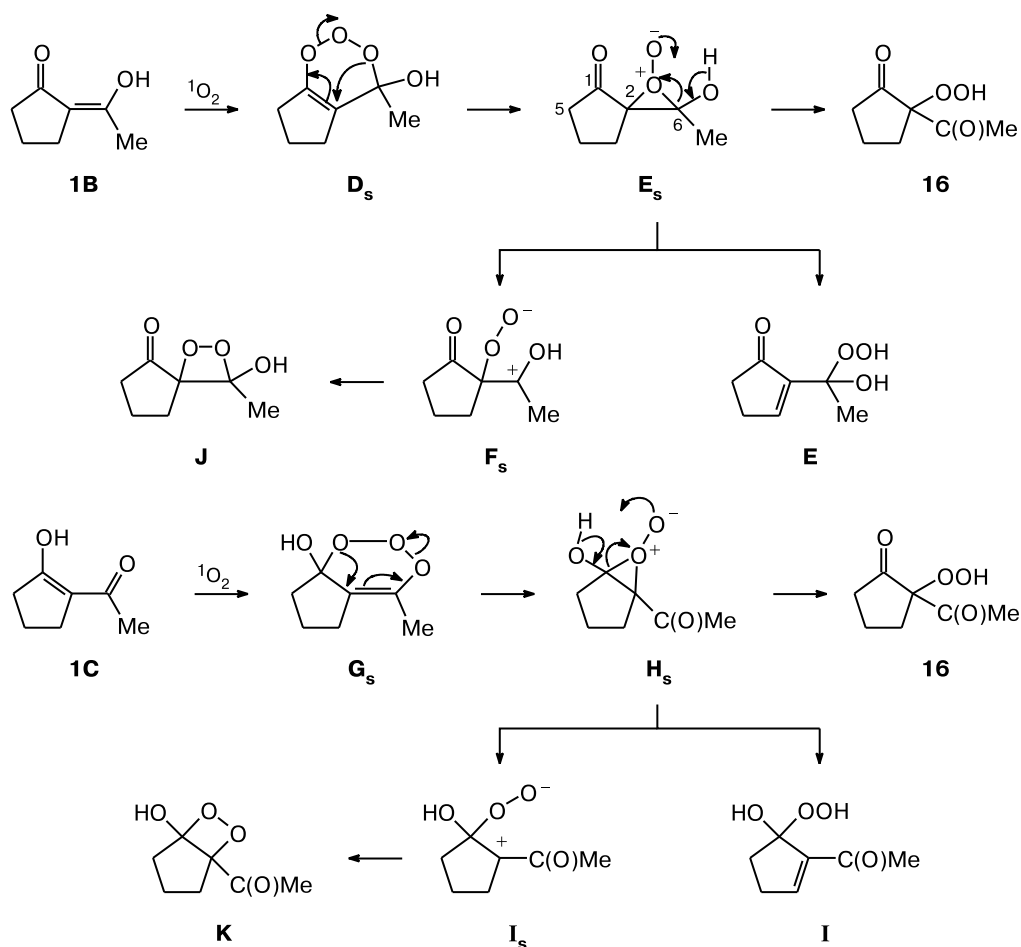
The initial steps of the photochemical oxidation of diketone **1** with molecular O₂ proceed in a different manner than the thermal oxidation.

The photoexcited O₂ molecule is predominantly exists in the singlet state and does not manifest properties of a biradical as a thermoexcited molecule, which is confirmed by the results of successful photooxidation of diketone **1** in the presence of ionol. The hypothesis about the formation of peroxy epoxide intermediates by the reactions of α,β-enones and enol forms of 1,3-dicarbonyl compounds with ¹O₂ advanced for the first time in Ref. 54 is presently commonly accepted.^{49–51,55,57}

It is most likely that the reaction of ¹O₂ with α,β-enones of types **1B** or **1C** should proceed⁵⁴ as [4+2] cycloaddition by analogy to the reactions of ¹O₂ with 1,3-dienes. The authors⁵⁴ did not explain why the possibility of [2+2] cycloaddition with the formation of the corresponding dioxetane intermediates is rejected. 1,2,3-Trioxines of type **D_s** (Scheme 7) (subscript *s* means that this intermediate is assigned to the reactions of singlet oxygen) and **G_s** that formed are further rearranged to peroxy epoxides of types **E_s** and **H_s**. The predominant direction of decomposition of zwitterion **E_s** is the C(6)—O bond cleavage of the three-membered ring, which should afford hydroperoxide **16**. The abstraction of the hydrogen atom from the C(3) atom of intermediate **E_s** (ene reaction) with the simultaneous cleavage of the C(2)—O bond of the three-membered ring can result in the formation of intermediate **E** (intermediate **H** in Scheme 2). Finally, the rearrangement of zwitterion **E_s** to zwitterion **F_s** followed by ring closure can result in dioxetane **J** (dioxetane **F** in Scheme 2). The transformations of peroxy epoxide **H_s**, giving hydroperoxide **16**, α-hydroxy hydroperoxide **I** (intermediate **I** in Scheme 2), and dioxetane **K** (dioxetane **G** in Scheme 2), should proceed similarly. The further transformations of intermediates **16**, **E**, **J**, **I**, and **K** were discussed above (see Schemes 2–6). The cleavage of the O—O bond of hydroperoxide **16** with the formation of radical **K** during the photochemical oxidation of diketone **1** (see Scheme 3) occurs, probably, under the action of relatively rigid UV irradiation.

The study performed shows that, under certain thermolysis and photolysis conditions, 2-acetylcyclopentanone (**1**) exhibits high activity towards atmospheric O₂, giving complicated mixtures of oxidation products. In some cases, they consist of 15 components. The major products of oxidative transformations of diketone **1** during both thermolysis and photolysis are 2-hydroxy-1,3-diketone **2** (yields 18–45%), 5,6-dioxoheptanoic acid (**11**), glutaric acid (**15**), 2-hydroxymethyl-1,3-dione (**3**), dimeric 1,3-diketone (**4**), 2-acetoxycyclopentanone (**6**), and glutaric anhydride (**7**). The yields of these compounds depend strongly on the conditions of substrate oxidation. The formation of 2-hydroxy-1,3-dione **2** is the first example of the direct α-hydroxylation of 1,3-dicarbonyl compound in a moderate yield under simpler conditions than the known ones. The side process of hydrogen peroxide formation due to the thermolysis of intermediate α-hydroxy hydroperoxides occurs during the oxidation of diketone **1** with atmospheric O₂. The presence of H₂O₂ and, possibly, peroxyacids formed by the reactions of H₂O₂ with carboxylic acids present in the reaction mixture results in such oxidation products as epoxide **5**, acetoxy ketone **6**, γ-lactone **8**, aceburic acid **12**, and pyruvic acid **13**. The obtained oxidation products and, first of all, dioxocarboxylic acid **11** are interesting as polyfunctional syntheses.

Scheme 7



Experimental

Melting points were determined on a Boetius heating stage and were not corrected. IR spectra were recorded on a Bruker Vector 22 spectrophotometer in a solution of $CHCl_3$. 1H and ^{13}C NMR spectra were measured on a Bruker Avance DPX-300 spectrometer (300.13 MHz for 1H and 75.47 MHz for ^{13}C) in a $CDCl_3$ solution using Me_4Si as an internal standard. Mass spectra (EI) were obtained on an AMD 604 S instrument (8 kW) with direct injection at ionization energies of 15 and 70 eV. Elemental analysis was carried out on a Flash EA1112 C,H,N analyzer. The reaction course and individual character of the synthesized compounds were monitored by TLC on Silufol UV-254 plates in benzene–acetone systems (from 15 : 1 to 2 : 1). Individual compounds were isolated from mixtures of reaction products on columns with SiO_2 (Alfa Aesar, 70–230 μm) eluting with hexane–acetone mixtures.

Freshly distilled 2-acetylcyclopentanone (Lancaster, Great Britain, b.p. 88–90 °C at 15 Torr, $[n]_D^{20}$ 1.4900) was used. Granulated $CaCl_2 \cdot 2H_2O$ (Russian Federation, GOST 4161-77, pure grade, the content of the main substance $\geq 98\%$) was powdered and dried in a porcelain cup at 145–150 °C for 3 h. Anhydrous solvents were prepared according to standard procedures.

A DRT-240-1 medium-pressure mercury lamp (Russian Federation) with a consumed power of 950 W was used for photochemical experiments.

Thermal oxidation of 2-acetylcyclopentanone (1) with atmospheric oxygen. Dried $CaCl_2$ (6.66 g, 0.06 mol) was added to a solution of diketone **1** (1.26 g, 0.01 mol) in anhydrous acetone (100 mL), and the mixture was refluxed for 30 h. The precipitate was separated and washed with anhydrous acetone (3×7 mL), and the combined filtrates were evaporated to dryness. The residue obtained contained formic, acetic, and pyruvic acids according to the data of 1H NMR spectra (δ for $HCOOH$: 9.76 (br.s, 2 H); for $AcOH$: 2.09 (s, 3 H, Me), 10.83 (s, 1 H, $COOH$); for $MeC(O)COOH$: 2.35 (s, 3 H, $COMe$), 10.91 (s, 1 H, $COOH$) and ^{13}C NMR (for $HCOOH$: 166.5; for $AcOH$: 20.9 (Me), 176.9 ($COOH$); for $MeCOCOHOH$: 26.8 (Me), 171.1 ($COOH$), and 184.2 (CO)) detected in $CDCl_3$ for unseparated mixtures of the oxidation products of diketone **1**. The data presented are well consistent with the spectral data of authentic samples of the acids. The obtained residue was dissolved in chloroform (50 mL), the acids were washed off with a saturated aqueous solution of $NaHCO_3$ (3×20 mL), and then the organic phase was washed with a saturated aqueous solution of $NaCl$ (3×15 mL) and dried above anhydrous Na_2SO_4 . The solvent was removed, and the residue was chromatographed on a column with SiO_2 . Elution

with a hexane—acetone (35 : 1) mixture gave 0.25 g (20%) of the starting diketone **1** as a colorless mobile liquid. IR, $\nu_{\max}/\text{cm}^{-1}$: 3530—2400 (OH), 1744 (C=O), 1709 (C=O), 1660 (C=O), 1610 (C=O, C=C), 1588 (C=O, C=C), 1451, 1405, 1387, 1360, 1285, 1239, 1197, 1180, 1139, 1121. $^1\text{H NMR}$ (CDCl_3), δ for enol form **1B** (**1C**): 1.91 (quint, 2 H, 2 H(4), $J = 7.1$ Hz); 1.99 (s, 3 H, C(6)Me); 2.41 (t, 2 H, 2 H(5), $J = 7.1$ Hz); 2.55 (t, 2 H, 2 H(3), $J = 7.1$ Hz); 13.50 (br.s, 1 H, OH). $^{13}\text{C NMR}$ (CDCl_3), δ for enol form **1B** (**1C**): 20.1 (C(4)); 20.6 (C(7)); 25.7 (C(3)); 36.8 (C(5)); 109.7 (C(2)); 175.7 (C(6)); 204.9 (C(1)). $^1\text{H NMR}$ (CDCl_3), δ for diketone form **1A**: 1.87 (m, 1 H, H(4)); 2.06 (m, 2 H, H(3), H(4)); 2.25 (m, 1 H, H(5)); 2.29 (m, 1 H, H(5)); 2.32 (s, 3 H, COMe); 2.42 (m, 1 H, H(3)); 3.39 (dd, 1 H, H(2), $J = 5.7$ Hz, $J = 8.1$ Hz). $^{13}\text{C NMR}$ (CDCl_3), δ for diketone form **1A**: 20.5 (C(4)); 25.0 (C(3)); 30.0 (C(7)); 38.6 (C(5)); 62.6 (C(2)); 202.3 (C(6)); 212.7 (C(1)).

Elution with a hexane—acetone (30 : 1) mixture gave 0.22 g (11%) of **1,1'-diacetyl-1,1'-bicyclopentyl-2,2'-dione** (**4**) as a colorless viscous oil. IR, $\nu_{\max}/\text{cm}^{-1}$: 1753 (C=O), 1712 (C=O), 1465, 1440, 1419, 1403, 1359, 1316, 1275, 1226, 1152, 1127. $^1\text{H NMR}$ (CDCl_3), δ : 2.00—2.15 (m, 2 H, 2 H(4)); 2.16—2.31 (m, 1 H, H(3)); 2.33—2.40 (m, 1 H, H(5)); 2.47 (s, 3 H, COMe); 2.48—2.59 (m, 1 H, H(5)); 2.76—2.87 (m, 1 H, H(3)). $^{13}\text{C NMR}$ (CDCl_3), δ : 18.9 (C(4)); 27.5 (C(7)); 36.3 (C(5)); 36.6 (C(3)); 74.2 (C(2)); 201.9 (C(6)); 208.1 (C(1)). MS (EI, 15 eV), m/z (I_{rel} (%)): 250 [$\text{M}]^+$ (5), 208 [$\text{M}]^+ - 42$ (28), 207 [$\text{M}]^+ - 43$ (7), 125 (40), 83 (37), 42 (100). Found (%): C, 67.29; H, 7.21. $\text{C}_{14}\text{H}_{18}\text{O}_4$. Calculated (%): C, 67.18; H, 7.25.

Elution with a hexane—acetone (25 : 1) mixture gave 0.007 g (~1%) of **1,3,5-trioxane** (**9**). Colorless crystals, m.p. 62—63 °C. $^1\text{H NMR}$ (CDCl_3), δ : 5.14 (s, 6 H, 3 CH_2). $^{13}\text{C NMR}$ (CDCl_3), δ : 95.4 (C(2), C(4), C(6)). MS (EI, 15 eV), m/z (I_{rel} (%)): 90 [$\text{M}]^+$ (6), 30 (100).

Elution with a hexane—acetone (20 : 1) mixture gave 0.064 g (7%) of **glutaric anhydride** (**7**). Colorless crystals, m.p. 51—54 °C. IR, $\nu_{\max}/\text{cm}^{-1}$: 1748 (C=O), 1715 (C=O), 1602, 1451, 1415, 1290, 1240, 1132. $^1\text{H NMR}$ (CDCl_3), δ : 2.02 (quint, 2 H, 2 H(4), $J = 6.8$ Hz); 2.75 (t, 4 H, 2 H(3), 2 H(5), $J = 6.8$ Hz). $^{13}\text{C NMR}$ (CDCl_3), δ : 16.7 (C(4)); 30.3 (C(3), C(5)); 166.8 (C(2), C(6)).

Elution with a hexane—acetone (15 : 1) mixture gave 0.014 g (2%) of **γ -butyrolactone** (**8**). Colorless liquid, $[\eta]_{\text{D}}^{20}$ 1.4351. IR, $\nu_{\max}/\text{cm}^{-1}$: 1772 (C=O). $^1\text{H NMR}$ (CDCl_3), δ : 2.23 (m, 2 H, 2 H(4)); 2.45 (m, 2 H, 2 H(3)); 4.35 (t, 2 H, 2 H(5), $J = 7.1$ Hz). $^{13}\text{C NMR}$ (CDCl_3), δ : 22.2 (C(4)); 27.8 (C(3)); 68.5 (C(5)); 177.8 (C(2)).

Elution with a hexane—acetone (10 : 1) mixture gave 0.023 g (2%) of **2-acetoxycyclopentanone** (**6**) as a colorless oil. IR, $\nu_{\max}/\text{cm}^{-1}$: 1756 (C=O), 1718 (C=O), 1405, 1356, 1232, 1209, 1158, 1092, 1049. $^1\text{H NMR}$ (CDCl_3), δ : 1.87—2.13 (m, 2 H, 2 H(4)); 2.14 (s, 3 H, OAc); 2.09—2.19 (m, 2 H, 2 H(5)); 2.16—2.27 (m, 2 H, 2 H(3)); 5.05 (m, 1 H, H(2), $J = 8.1$ Hz, $J = 4.1$ Hz, $J = 3.8$ Hz, $J = 2.2$ Hz). $^{13}\text{C NMR}$ (CDCl_3), δ : 17.2 (C(4)); 20.9 (C(7)); 28.5 (C(3)); 34.4 (C(5)); 75.8 (C(2)); 170.4 (C(6)); 215.0 (C(1)). MS (EI, 70 eV), m/z (I_{rel} (%)): 142 [$\text{M}]^+$ (10), 100 (100), 99 (85), 98 (21), 83 (6), 82 (17), 73 (6), 72 (16), 71 (34), 60 (14), 55 (18), 44 (39).

Elution with a hexane—acetone (8 : 1) mixture gave 0.43 g (38%) of **2-acetyl-2-hydroxycyclopentanone** (**2**) as a colorless viscous oil (cf. Ref. 26: yellow oil; Ref. 27: white solid, m.p. 58—59 °C). IR (CHCl_3), $\nu_{\max}/\text{cm}^{-1}$: 3511 (OH), 1753 (C=O), 1711 (C=O), 1402, 1360, 1227, 1157, 1092, 1048. IR (CCl_4),

$\nu_{\max}/\text{cm}^{-1}$: 3520 (OH), 3476 (OH), 1755 (C=O), 1747 (C=O), 1718 (C=O), 1711 (C=O), 1405, 1356, 1315, 1232, 1209, 1158, 1092, 1049, 1026. $^1\text{H NMR}$ (CDCl_3), δ : 1.94—2.05 (m, 1 H, H(3)); 2.06—2.20 (m, 2 H, 2 H(4)); 2.23 (s, 3 H, COMe); 2.40—2.50 (m, 3 H, H(3), 2 H(5)); 3.93 (br.s, 1 H, OH). $^{13}\text{C NMR}$ (CDCl_3), δ : 18.4 (C(4)); 25.7 (C(7)); 34.7 (C(3)); 36.0 (C(5)); 86.3 (C(2)); 207.2 (C(6)); 215.2 (C(1)). MS (EI, 70 eV), m/z (I_{rel} (%)): 142 [$\text{M}]^+$ (7), 125 (5), 124 (2), 115 (16), 114 (22), 100 (39), 99 (28), 88 (10), 87 (34), 86 (100), 85 (25), 83 (10), 74 (10), 73 (37), 71 (44), 70 (13), 69 (12), 60 (76), 58 (45), 57 (23), 55 (88), 46 (39), 45 (13), 44 (94), 43 (47), 42 (34), 40 (18), 32 (53), 31 (30).

Elution with a hexane—acetone (7 : 1) mixture gave 0.022 g (2%) of **2-acetyl-2,3-epoxycyclopentanone** (**5**) as a colorless viscous oil. IR, $\nu_{\max}/\text{cm}^{-1}$: 1754 (C=O), 1710 (C=O), 1446, 1411, 1389, 1360, 1301, 1284, 1257, 1216, 1165, 1072, 1040. $^1\text{H NMR}$ (CDCl_3), δ : 2.14 (m, 1 H, H(4)); 2.23 (m, 2 H, 2 H(5)); 2.28 (s, 3 H, COMe); 2.38 (m, 1 H, H(4)); 4.11 (br.s, 1 H, H(3), $\Sigma J = 2.2$ Hz). $^{13}\text{C NMR}$ (CDCl_3), δ : 22.7 (C(4)); 28.3 (C(7)); 32.8 (C(5)); 63.9 (C(2)); 65.8 (C(3)); 199.5 (C(6)); 204.6 (C(1)). MS (EI, 70 eV), m/z (I_{rel} (%)): 140 [$\text{M}]^+$ (15), 126 (22), 125 (29), 124 (25), 111 (16), 109 (31), 98 (8), 97 (11), 96 (11), 85 (16), 81 (7), 57 (17), 55 (34), 45 (25), 44 (63), 43 (14), 42 (22), 32 (100).

Elution with a hexane—acetone (5 : 1) mixture gave 0.062 g (5%) of **2-acetyl-2-hydroxymethylcyclopentanone** (**3**) as a colorless oil. IR, $\nu_{\max}/\text{cm}^{-1}$: 3612 (OH), 3519 (OH), 1739 (C=O), 1708 (C=O), 1406, 1358, 1318, 1276, 1243, 1149, 1060. $^1\text{H NMR}$ (CDCl_3), δ : 1.96 (m, 1 H, H(4)); 1.98 (m, 1 H, H(3)); 2.01 (m, 1 H, H(5)); 2.23 (s, 3 H, COMe); 2.26 (m, 1 H, H(4)); 2.37 (m, 1 H, H(3)); 2.43 (m, 1 H, H(5)); 3.84 (d, 1 H, H(8), $J = 11.3$ Hz); 3.91 (d, 1 H, H(8), $J = 11.3$ Hz). $^{13}\text{C NMR}$ (CDCl_3), δ : 19.8 (C(4)); 27.1 (C(7)); 29.8 (C(3)); 39.1 (C(5)); 64.8 (C(8)); 69.8 (C(2)); 205.8 (C(6)); 216.9 (C(1)). MS (EI, 70 eV), m/z (I_{rel} (%)): 156 [$\text{M}]^+$ (11), 139 (7), 138 (15), 115 (30), 114 (12), 111 (13), 110 (15), 97 (25), 96 (96), 95 (26), 87 (44), 68 (77), 67 (25), 55 (42), 46 (31), 44 (100), 43 (26), 42 (43). Found (%): C, 61.61; H, 7.78. $\text{C}_8\text{H}_{12}\text{O}_3$. Calculated (%): C, 61.52; H, 7.74.

Elution with a hexane—acetone (4 : 1) mixture gave 0.014 g of **4-hydroxy-4-methylpentan-2-one** (diacetone alcohol, **10**). Colorless labile liquid, $[\eta]_{\text{D}}^{20}$ 1.4232. IR, $\nu_{\max}/\text{cm}^{-1}$: 3540 (OH), 1710 (C=O), 1542, 1508, 1457, 1389, 1377, 1362, 1325, 1175, 1146, 1017. $^1\text{H NMR}$ (CDCl_3), δ : 1.21 (s, 6 H, 2 C(4)Me); 1.79 (br.s, 1 H, OH); 2.14 (s, 3 H, COMe); 2.60 (s, 2 H, CH_2). $^{13}\text{C NMR}$ (CDCl_3), δ : 29.5 (C(5), C(6)); 32.1 (C(1)); 54.2 (C(3)); 69.7 (C(4)); 211.3 (C(2)).

An aqueous soda solution (60 mL) remained after washing of the organic extract was acidified with 2 M HCl to pH 1.0, and the reaction products were extracted with chloroform (5 × 10 mL). The combined organic extracts were washed with a saturated aqueous solution of NaCl (4 × 5 mL) and dried above Na_2SO_4 . The solvent was removed and the unpurified product was chromatographed on a column with SiO_2 . Elution with a hexane—acetone (6 : 1) mixture gave 0.164 g (13%) of **5,6-dioxoheptanoic acid** (**11**). Viscous light yellow oil. IR, $\nu_{\max}/\text{cm}^{-1}$: 3400—2400 (COOH), 1745 (C=O), 1714 (C=O), 1417, 1358, 1239, 1133, 1046. $^1\text{H NMR}$ (CDCl_3), δ : 1.94 (quint, 2 H, 2 H(3), $J = 7.2$ Hz); 2.34 (s, 3 H, COMe); 2.43 (t, 2 H, 2 H(2), $J = 7.2$ Hz); 2.85 (t, 2 H, 2 H(4), $J = 7.2$ Hz); 9.82 (br.s, 1 H, COOH). $^{13}\text{C NMR}$ (CDCl_3), δ : 18.3 (C(3)); 24.0 (C(7)); 33.0

(C(2)); 35.1 (C(4)); 178.9 (C(1)); 197.6 (C(6)); 198.6 (C(5)). MS (EI, 70 eV), m/z (I_{rel} (%)): 158 [M]⁺ (1), 141 (2), 140 (1), 116 (3), 115 (43), 114 (4), 112 (2), 101 (2), 100 (3), 98 (2), 97 (5), 87 (37), 86 (14), 85 (7), 73 (6), 69 (5), 60 (8), 58 (4), 55 (24), 46 (29), 45 (3), 44 (100), 43 (13), 42 (17), 32 (5), 31 (7). Found (%): C, 53.24; H, 6.35. C₇H₁₀O₄. Calculated (%): C, 53.16; H, 6.37.

Elution with a hexane—acetone (5 : 1) mixture gave 0.023 g (2%) of **4-acetoxybutyric (aceburic) acid (12)** as a colorless oil. IR, $\nu_{\text{max}}/\text{cm}^{-1}$: 3400—2600 (COOH), 1728 (C=O), 1717 (C=O), 1710 (C=O). ¹H NMR (CDCl₃), δ : 1.99 (m, 2 H, 2 H(3), $J = 6.3$ Hz, $J = 7.2$ Hz); 2.06 (s, 3 H, OAc); 2.47 (t, 2 H, 2 H(2), $J = 7.2$ Hz); 4.13 (t, 2 H, 2 H(4), $J = 6.3$ Hz). ¹³C NMR (CDCl₃), δ : 21.2 (C(6)); 24.1 (C(3)); 30.8 (C(2)); 63.6 (C(4)); 171.1 (C(5)); 179.0 (C(1)).

Elution with a hexane—acetone (3 : 1) mixture gave 0.074 g (7%) of **glutaric acid (15)**. Colorless crystals, m.p. 97—98 °C. IR, $\nu_{\text{max}}/\text{cm}^{-1}$: 3400—2370 (COOH), 1715 (C=O). ¹H NMR (CDCl₃), δ : 2.01 (quint, 2 H, 2 H(3), $J = 6.7$ Hz); 2.46 (t, 4 H, 2 H(2), 2 H(4), $J = 6.7$ Hz); 10.30 (br.s, 2 H, 2 OH). ¹³C NMR (CDCl₃), δ : 20.1 (C(3)); 33.3 (C(2), C(4)); 178.7 (C(1), C(5)).

Elution with a hexane—acetone (2 : 1) mixture gave 0.009 g (~1%) of **succinic acid (14)**. Colorless crystals, m.p. 181—183 °C. IR, $\nu_{\text{max}}/\text{cm}^{-1}$: 3420—2380 (COOH), 1714 (C=O). ¹H NMR (CDCl₃), δ : 2.72 (s, 4 H, 2 CH₂); 10.11 (br.s, 2 H, 2 OH). ¹³C NMR (acetone-*d*₆), δ : 29.1 (C(2), C(3)); 173.9 (C(1), C(4)).

Photochemical oxidation of 2-acetylcyclopentanone (1) with atmospheric oxygen in acetone. A solution of diketone **1** (1.26 g, 0.01 mol) in anhydrous acetone (100 mL) was irradiated for 6 h in a conic quartz flask with stirring. The solvent was removed, and the residue was dissolved in chloroform (50 mL) and treated as described above. The overall neutral fraction was chromatographed on a column with SiO₂. Elution with a hexane—acetone (25 : 1) mixture gave 0.014 g (2%) of **1,3,5-trioxane (9)** identical to that described above.

Elution with a hexane—acetone (20 : 1) mixture gave 0.046 g (5%) of **glutaric anhydride (7)** identical to that described above.

Elution with a hexane—acetone (15 : 1) mixture gave 0.028 g (4%) of **γ -butyrolactone (8)** identical to that described above.

Elution with a hexane—acetone (10 : 1) mixture gave 0.023 g (2%) of **2-acetoxycyclopentanone (6)** identical to that described above.

Elution with a hexane—acetone (8 : 1) mixture gave 0.204 g (18%) of **2-acetyl-2-hydroxycyclopentanone (2)** identical to that described above.

Elution with a hexane—acetone (7 : 1) mixture gave 0.033 g (3%) of **2-acetyl-2,3-epoxycyclopentanone (5)** identical to that described above.

Elution with a hexane—acetone (5 : 1) mixture gave 0.372 g (30%) of **2-acetyl-2-hydroxymethylcyclopentanone (3)** identical to that described above.

The acidic fraction was separated on a column with SiO₂. Elution with a hexane—acetone (3 : 1) mixture gave 0.180 g (17%) of **glutaric acid (15)** identical to that described above.

Elution with a hexane—acetone (2 : 1) mixture gave 0.009 g (1%) of **succinic acid (14)** identical to that described above.

Photochemical oxidation of 2-acetylcyclopentanone (1) with atmospheric oxygen in CCl₄. A solution of diketone **1** (1.26 g, 0.01 mol) in anhydrous CCl₄ (100 mL) was irradiated for 4.5 h.

The solvent was removed, and the residue was separated into the neutral and acidic fraction as described above. The overall neutral fraction was chromatographed on a column with SiO₂. Elution with a hexane—acetone (30 : 1) mixture gave 0.04 g (2%) of **dimer (4)** identical to that described above.

Elution with a hexane—acetone (20 : 1) mixture gave 0.109 g (12%) of **glutaric anhydride (7)** identical to that described above.

Elution with a hexane—acetone (15 : 1) mixture gave 0.015 g (2%) of **γ -butyrolactone (8)** identical to that described above.

Elution with a hexane—acetone (10 : 1) mixture gave 0.034 g (3%) of **2-acetoxycyclopentanone (6)** identical to that described above.

Elution with a hexane—acetone (8 : 1) mixture gave 0.362 g (32%) of **2-acetyl-2-hydroxycyclopentanone (2)** identical to that described above.

Elution with a hexane—acetone (7 : 1) mixture gave 0.034 g (3%) of **2-acetyl-2,3-epoxycyclopentanone (5)** identical to that described above.

The acidic fraction was separated on a column with SiO₂. Elution with a hexane—acetone (6 : 1) mixture gave 0.151 g (12%) of **5,6-dioxoheptanoic acid (11)** identical to that described above.

Elution with a hexane—acetone (3 : 1) mixture gave 0.317 g (30%) of **glutaric acid (15)** identical to that described above.

Elution with a hexane—acetone (2 : 1) mixture gave 0.018 g (2%) of **succinic acid (14)** identical to that described above.

Photochemical oxidation of 2-acetylcyclopentanone (1) with atmospheric oxygen in acetone in the presence of ionol. A solution of diketone **1** (1.26 g, 0.01 mol) and ionol (0.22 g, 0.001 mol) in anhydrous acetone (100 mL) was irradiated for 7.5 h. The solvent was removed, and the residue was separated into the neutral and acidic fraction. The overall neutral fraction was chromatographed on a column with SiO₂. Elution with a hexane—acetone (15 : 1) mixture gave 0.021 g (3%) of **γ -butyrolactone (8)** identical to that described above.

Elution with a hexane—acetone (10 : 1) mixture gave 0.046 g (4%) of **2-acetoxycyclopentanone (6)** identical to that described above.

Elution with a hexane—acetone (8 : 1) mixture gave 0.306 g (27%) of **2-acetyl-2-hydroxycyclopentanone (2)** identical to that described above.

Elution with a hexane—acetone (5 : 1) mixture gave 0.347 g (28%) of **2-acetyl-2-hydroxymethylcyclopentanone (3)** identical to that described above.

The acidic fraction was separated on a column with SiO₂. Elution with a hexane—acetone (6 : 1) mixture gave 0.051 g (4%) of **5,6-dioxoheptanoic acid (11)** identical to that described above.

Elution with a hexane—acetone (5 : 1) mixture gave 0.024 g (2%) of **4-acetoxybutyric acid (12)** identical to that described above.

Elution with a hexane—acetone (3 : 1) mixture gave 0.328 g (31%) of **glutaric acid (15)** identical to that described above.

Photochemical oxidation of 2-acetylcyclopentanone (1) with atmospheric oxygen in CCl₄ in the presence of ionol. A solution of diketone **1** (1.26 g, 0.01 mol) and ionol (0.22 g, 0.001 mol) in anhydrous CCl₄ (100 mL) was irradiated for 3.5 h. The solvent was removed, and the residue was separated into the neutral and acidic fraction. The overall neutral fraction was chromatographed on a column with SiO₂. Elution with a hexane—acetone

(15 : 1) mixture gave 0.007 g (1%) of γ -butyrolactone (**8**) identical to that described above.

Elution with a hexane—acetone (10 : 1) mixture gave 0.195 g (17%) of 2-acetoxycyclopentanone (**6**) identical to that described above.

Elution with a hexane—acetone (8 : 1) mixture gave 0.509 g (45%) of 2-acetyl-2-hydroxycyclopentanone (**2**) identical to that described above.

The acidic fraction was separated on a column with SiO₂. Elution with a hexane—acetone (6 : 1) mixture gave 0.227 g (18%) of 5,6-dioxoheptanoic acid (**11**) identical to that described above.

Elution with a hexane—acetone (3 : 1) mixture gave 0.095 g (9%) of glutaric acid (**15**) identical to that described above.

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