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Short Note

1-(((6-(Methoxycarbonyl)-5-oxononan-4-yl)oxy)carbonyl) cyclopropane-1-carboxylic Acid

Evgenii S. Gorlov [1], Diana V. Shuingalieva [1,2,3], Alexey I. Ilovaisky [1,3], Vera A. Vil' [1,3,*] and Alexander O. Terent'ev [1,3,*]

1 N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prospect, Moscow 119991, Russia
2 Faculty of Engineering Chemical Technology, D. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya Square, Moscow 125047, Russia
3 All-Russian Research Institute for Phytopathology, B. Vyazyomy, Moscow 143050, Russia
* Correspondence: vil@ioc.ac.ru (V.A.V.); terentev@ioc.ac.ru (A.O.T.)

Abstract: Here, we first report the 2′-acyloxy-1,3-dicarbonyl compound construction in a three-component oxidative reaction of alkyl ketene dimer with cyclic diacyl peroxide and trimethyl orthoformate. The discovered synthesis allows us to form 2′-functionalized 1,3-dicarbonyl compounds instead of the common 2-functionalized moiety. The reaction between 4-butylidene-3-propyloxetan-2-one and cyclopropyl malonoyl peroxide proceeds in the presence of trifluoroacetic acid and trimethyl orthoformate at 120 °C for 1 h. The synthesized compound was characterized by NMR spectroscopy, mass spectrometry, and IR spectroscopy.

Keywords: alkyl ketene dimer; peroxides; cyclic diacyl peroxide; oxidation; oxidative coupling

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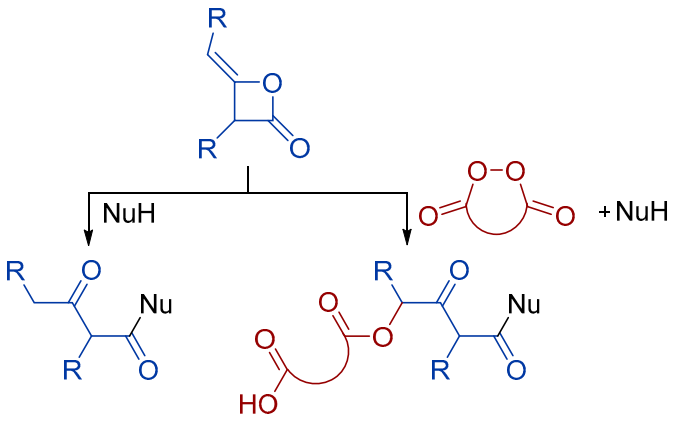
1. Introduction

Alkyl ketene dimers were first synthesized in 1901 [1] and their reactivity is mostly determined by a strained oxetan-2-one ring, which readily reacts with various nucleophiles [2–6] (Scheme 1). Also, alkyl ketene dimers can be regarded as acyl enolates. However, there are only scattered reports on metal-catalyzed oxidation of diketene [7–9], and there is only one example of metal-free oxidation by ozone [10,11]. So, further investigation of oxidative transformations of ketene dimers would be desirable. Our idea is that such a transformation is possible using cyclic diacyl peroxides as oxidants (Scheme 1).



Scheme 1. The core fragment of alkyl ketene dimers and its reactivity.

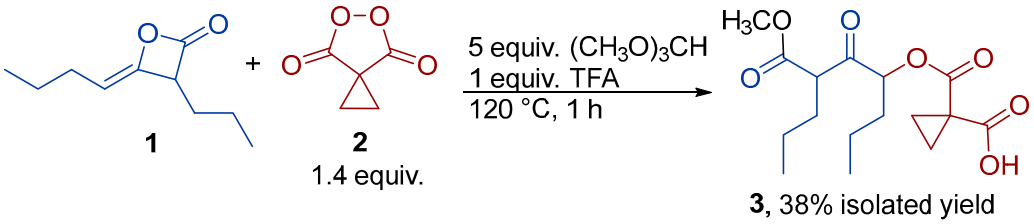
Cyclic diacyl peroxides were first synthesized in the 1950s [12,13], and their chemical properties are still being intensively studied [14,15]. A search for new interesting structures based on cyclic diacyl peroxides continues as well, and recently a doubled cyclic diacyl

peroxide has been reported that may be useful for polymer chemistry [16]. Cyclic diacyl peroxides are utilized in dihydroxylation, dioxygenation [17–23], and oxyamination [24] of alkenes. Oxyfunctionalization of arenes [25–31] as well as arene dearomatization [32] were achieved using these peroxides. Oxidative acyloxylation of dicarbonyl compounds [33], heterocycles [34], and the derivatives of monocarbonyl compounds [35,36] also were developed. Recently, our group reported on the reaction of enol acetates with cyclic diacyl peroxides, which proceeds as a nucleophilic substitution of an oxygen atom (S_N2@O) [37] and Ni-catalyzed C(sp^3)-H acyloxylation [38,39] with such reagents. Here, we report the 2′-acyloxy-1,3-dicarbonyl compound construction in a three-component oxidative reaction of alkyl ketene dimer with cyclic diacyl peroxide and trimethyl orthoformate.

2. Results and Discussion

4-Butylidene-3-propyloxetan-2-one **1** and cyclopropyl malonoyl peroxide **2** were chosen to study the oxidation of alkyl ketene dimers with cyclic diacyl peroxides. Moreover, an important component of the reaction is a nucleophile, whose role is to intercept the supposed unstable intermediate. Since cyclic diacyl peroxide **2** can react with the nucleophile, the choice of nucleophile is not trivial. Alkyl ketene dimers, being acylating agents, are also labile to a nucleophilic attack. Thus, the nucleophile must be inert towards the peroxide and the alkyl ketene dimer, and it must be able to react with the intermediate at the same time.

Surprisingly, when trimethyl orthoformate was used as the nucleophile, and TFA as a source of protons, product **3** was obtained with the NMR yield of 43% (Scheme 2). The reaction was completed in 1 hour in a sealed vessel at 120 °C.

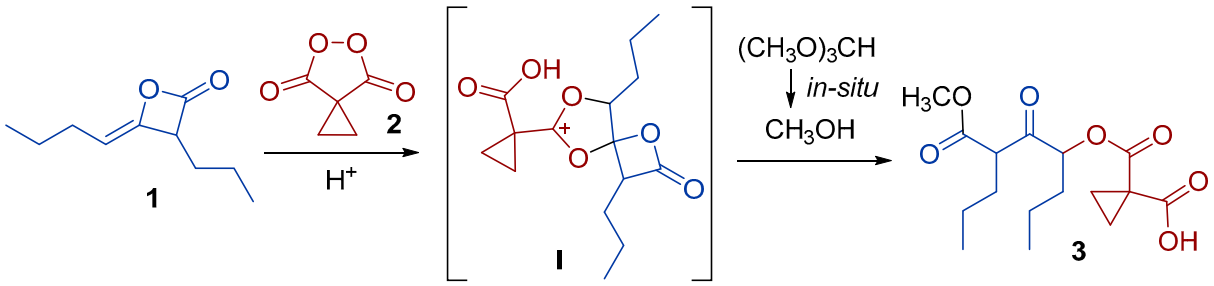


Scheme 2. Oxidation of alkyl ketene dimer **1** with cyclic diacyl peroxide **2** in the presence of trimethyl orthoformate.

To our delight, there was no further oxidation of **3** by cyclopropyl malonoyl peroxide **2**, despite the possibility of such a process, which was described in the literature [33]. Product **3** was isolated as a mixture of two diastereomers in a ratio of 50:50 using column chromatography. Interestingly, one of the diastereomers predominates right after the reaction, but during the work-up, the mixture is racemized, probably due to keto-enol tautomerism. The mixture of diastereomers **3** was characterized by NMR, IR spectroscopy, and mass spectrometry (Figures S5–S8, Supplementary Materials). The ^{1}H NMR spectrum of compound **3** showed signals for two methyne protons at δ 5.35, 5.21 (both dd, 1H, C(O)C*H*(O)CH_2) and δ 3.59 (dt, 1H, C(O)CHC(O)), signals of CH_3O group at δ 3.75, 3.70 (both s, 3H), as well as three multiples related to CH_2 and CH_2CH_3 protons at δ 1.98–1.69 (m, 8H), 1.40–1.23 (m, 4H), 0.97–0.88 (m, 6H). The ^{13}C NMR spectra of compound **3** showed double sets of signals for most of the atoms. The analysis of the carbon resonances revealed the presence of two signals for C=O (δ 200.5, 199.8), signals for three ester fragments (δ 175.4; 170.3; 169.1, 168.9), two signals for one oxygenated tertiary carbon (δ 79.6, 79.0). Additionally, the close signals of sp^3 tertiary carbon and OCH_3 group were detected (δ 55.4, 54.8; 52.9, 52.7).

The plausible mechanism for the three-component oxidative reaction of alkyl ketene dimer with cyclic diacyl peroxide and trimethyl orthoformate was proposed based on the above-mentioned results and the data (Scheme 3) [20–27,33–39]. Initially, the nucleophilic attack of the C=C double bond of alkyl ketene dimer **1** to cyclic diacyl peroxide **2** leads to the formation of intermediate **I**. Then, it can be assumed that either a direct interaction of

trimethyl orthoformate with intermediate **I** occurs, or methanol is generated in situ and then is added to intermediate **I** to form the final product **3**.



Scheme 3. Proposed mechanism of oxidation of alkyl ketene dimer **1** with cyclic diacyl peroxide **2** in the presence of trimethyl orthoformate.

3. Materials and Methods

3.1. General Information

Caution: Peroxides are high-energy compounds. All reactions using these substances should be conducted within a fume hood and behind a safety shield. These procedures should be carried out by knowledgeable laboratory workers.

NMR spectra were recorded on commercial instruments (300.13 MHz for 1H, 75.48 MHz for 13C) in $CDCl_3$. The IR spectrum was recorded with a Bruker (Moscow, Russia) "Alpha-T" instrument. High-resolution mass spectrum (HRMS) was measured using electrospray ionization (ESI-TOF) [40]. The measurement was carried out in a positive ion mode (interface capillary voltage—4500 V); mass range from m/z 50 to m/z 1600 Da; and external/internal calibration was done with an electrospray calibrant solution. A syringe injection was used for solutions in CH_3CN (flow rate 3 µL/min). Nitrogen was applied as a dry gas; the interface temperature was set at 180 °C. The TLC analysis was carried out on standard silica gel chromatography plates. Silica gel was calcined in a vacuum oven at 200 °C for 2 h before use.

*3.2. Synthesis of 4-Butylidene-3-propyloxetan-2-one (**1**)*

Compound **1** was synthesized according to the modified literature method [41].

A solution of triethylamine (2.13 g, 21.0 mmol) in 10 mL of diethyl ether was added to a solution of valeroyl chloride (2.41 g, 20.0 mmol), whilst being stirred, in diethyl ether (10 mL) over 1 hour at 0 °C. The resulting solution was stirred for 24 h at room temperature. Then, the solution was filtered and a precipitate was washed with diethyl ether (2 × 20 mL). A filtrate was concentrated under reduced pressure using a rotary evaporator (15–20 mmHg, a water bath temperature ca. 20–25 °C). A residue was transferred on the top of chromatographic column and product **1** was isolated by column chromatography on SiO_2 (see Section 3.1 General Information) (the gradient system PE:EtOAc = 40:1). Product **1** was obtained as a colorless liquid (0.91 g, 5.43 mmol, 54% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.69 (t, J = 7.7 Hz, 1H), 3.94 (t, J = 7.2 Hz, 1H), 2.10 (q, J = 7.2 Hz, 2H), 1.76 (q, J = 7.7, 7.2 Hz, 2H), 1.55–1.37 (m, 4H), 0.96 (t, J = 6.9 Hz, 3H), 0.91 (t, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 145.9, 101.5, 53.7, 29.7, 26.8, 22.7, 19.9, 13.8, 13.7.

The data are fully consistent with those previously published [42].

*3.3. Synthesis of Cyclopropyl Malonoyl Peroxide (**2**)*

The cyclopropyl malonoyl peroxide (**2**) was synthesized according to the method in the literature [27]. The data are fully consistent with those previously published [27].

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.09 (s, 4H).

^{13}C NMR (76 MHz, $CDCl_3$); δ 172.3, 23.8, 19.9.

*3.4. Synthesis of 1-(((6-(Methoxycarbonyl)-5-oxononan-4-yl)oxy)carbonyl)cyclopropane-1-carboxylic acid (**3**)*

Trifluoroacetic acid (114.0 mg, 1.0 mmol) was added to a mixture of 4-butylidene-3-propyloxetan-2-one (**1**) (168.0 mg, 1.0 mmol), cyclopropyl malonoyl peroxide (**2**) (179.0 mg, 1.4 mmol), and trimethyl orthoformate (530.0 mg, 5.0 mmol). The reaction mixture was stirred in a sealed vessel for 1 hour at 120 °C. Then, the mixture was diluted with diethyl ether (5 mL) and transferred to a flask to concentrate under reduced pressure using a rotary evaporator (15–20 mmHg, a water bath temperature ca. 40 °C). A residue was transferred on the top of chromatographic column and product **3** was isolated by column chromatography on SiO_2 (the gradient system PE:EtOAc from 8:1 to 2:1 with 0.5 % AcOH). Product **3** was obtained as a colorless oil (124.0 mg, 0.38 mmol, 38% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.35 (dd, *J* = 8.8, 3.7 Hz), 5.21 (dd, *J* = 8.5, 3.9 Hz) (total 1H), 3.79–3.70 (m, 3H), 3.59 (dt, *J* = 12.0, 7.5 Hz, 1H), 1.98–1.69 (m, 8H), 1.40–1.23 (m, 4H), 0.97–0.88 (m, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.5, 199.8, 175.4, 170.3, 169.1, 168.9, 79.6, 79.0, 55.4, 54.8, 52.9, 52.7, 31.8, 31.6, 31.1, 29.7, 25.41, 25.37, 23.3, 22.3, 22.0, 20.8, 20.6, 18.8, 18.6, 13.9, 13.7.

HRMS (ESI-TOF) *m*/*z* [M+Na]$^+$. Calcd for $[C_{16}H_{24}O_7Na]^+$: 351.1414. Found: 351.1415.

IR (KBr), ν, cm^{-1}: 3122 (COO-H), 2963 (C-H), 2876 (C-H), 1727 (C=O), 1437, 1381, 1332, 1269, 1240, 1194, 1159, 1048, 977, 865, 820, 737, 677, 519.

4. Conclusions

The 2′-acyloxy-1,3-dicarbonyl compound was obtained in a three-component oxidative reaction of alkyl ketene dimer with cyclic diacyl peroxide and trimethyl orthoformate in a 38% isolated yield. The reaction between 4-butylidene-3-propyloxetan-2-one and cyclopropyl malonoyl peroxide to form 1-(((6-(methoxycarbonyl)-5-oxononan-4-yl)oxy)carbonyl)cyclopropane-1-carboxylic acid proceeds in the presence of trifluoroacetic acid and trimethyl orthoformate at 120 °C for 1 h. The chemistry of ketene dimers has been extended by the use of cyclic diacyl peroxides.

Supplementary Materials: The following supporting information can be downloaded online: Figure S1. ^{1}H NMR spectrum of 4-butylidene-3-propyloxetan-2-one (**1**); Figure S2. ^{13}C NMR spectrum of 4-butylidene-3-propyloxetan-2-one (**1**); Figure S3. ^{1}H NMR spectrum of cyclopropyl malonoyl peroxide (**2**); Figure S4. ^{13}C NMR spectrum of cyclopropyl malonoyl peroxide (**2**); Figure S5. ^{1}H NMR spectrum of 1-(((6-(methoxycarbonyl)-5-oxononan-4-yl)oxy)carbonyl)cyclopropane-1-carboxylic acid (**3**); Figure S6. ^{13}C NMR spectrum of 1-(((6-(methoxycarbonyl)-5-oxononan-4-yl)oxy)carbonyl)cyclopropane-1-carboxylic acid (**3**); Figure S7. IR spectrum of 1-(((6-(methoxycarbonyl)-5-oxononan-4-yl)oxy)carbonyl) cyclopropane-1-carboxylic acid (**3**); Figure S8. HRMS spectrum of 1-(((6-(methoxycarbonyl)-5-oxononan-4-yl)oxy)carbonyl)cyclopropane-1-carboxylic acid (**3**).

Author Contributions: D.V.S. conducted the experiments and analyzed the data; E.S.G. designed the study and the experiments and analyzed the data; V.A.V. designed the study and wrote the manuscript; A.I.I. reviewed and edited the final manuscript to publish; A.O.T. supervised the progress of work and reviewed and edited the final manuscript to publish. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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