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Very Important Publication

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C-O coupling of malonyl peroxides with enol ethers *via* [5+2] cycloaddition: non-Rubottom oxidation

Vera A. Vil' [a], Evgenii S. Gorlov [a,b], Oleg V. Bityukov [a], Yana A. Barsegyan [a], Yulia E. Romanova [a,b], Valentina M. Merkulova [a] and Alexander O. Terent'ev [a,b]*

[a] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prospect, Moscow, 119991, Russian Federation. E-mail: alterex@yandex.ru, terentev@ioc.ac.ru

[b] D. I. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya Square, Moscow, 125047, Russian Federation.

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Abstract. Malonyl peroxides act both as oxidants and reagents for C–O coupling in reactions with methyl and silyl enol ethers. In the proposed conditions, the oxidative C-O coupling of malonyl peroxides with enol ethers selectively proceeds, bypassing the traditional Rubottom hydroxylation of enol ethers by peroxides. It was observed that the oxidative [5+2] cycloaddition of malonyl peroxides and enol ethers is the key stage of the discovered process. Oxidative C-O coupling of silyl enol ethers leads to the formation of α-acyloxyketones with a free carboxylic acid group. A specially developed preparative one-pot procedure transforms ketones *via* silyl enol ethers formation and the following coupling into α-acyloxyketones with yields 35-88%. The acid-catalyzed coupling with methyl enol ethers gives remarkable products while retaining the easily oxidizable enol fragment. Furthermore, these molecules contain a free carboxylic acid group, thus these nontrivial products contain two usually incompatible acid and enol ether groups.

Keywords: Oxidation; Cross-coupling; Peroxides; Ketones; Enols

Introduction

The construction of chemical bonds by oxidative cross-coupling (cross-dehydrogenative coupling) is a promising and thriving field of modern organic chemistry. The formation of a new bond occurs with high atom efficiency and no functional groups are required.[1] Recently we reported efficient methods for oxidative C–O coupling of β-dicarbonyl[2] and N-heterocyclic[3] compounds with diacyl peroxides, in which one of the reagents, diacyl peroxide, acts both as an O-component and as an oxidizing agent. Cyclic diacyl peroxides firstly prepared in the 1950s[4] were rediscovered a few years ago,[5] when previously practically unavailable reactions stereoselective syn-[6] and anti-dihydroxylation[7] of alkenes, arene oxidation,[8] alkene oxyamination,[9] and dioxygenation,[10] Hofmann–Löffler–Freytag-type reaction,[11] selective sulfide oxidation,[12] peracids formation,[13] ring opening/halogenation of cycloalkanols,[14] and the [3 + 2] cycloaddition of arynes to azides[15] were realized. High oxidative ability, cyclic structure and absence of an acidic proton attached to the peroxide group favorably differ malonyl peroxides from related oxidants — peracids and noncyclic diacyl peroxides. These fundamental differences determine a wide range of unusual chemical properties of malonyl peroxides: instead of oxygenation, an oxygen atom of the malonyl peroxide links together the two molecules forming a product. The absence of an acidic proton prevents acid-catalyzed side processes.

The main approaches to oxidation of double bond by oxygen-containing oxidizers[16] are [2+2] cycloaddition of singlet oxygen resulted in dioxetanes,[17] ozonolysis providing ozonides[18] and processes including oxidation by oxygen-based systems,[19] oxaziridines,[20] inorganic oxygen-containing oxidizers,[21] peracids,[22] dioxiranes,[23] and systems based on ROOH[24] (Scheme 1). In this study we disclosed power of oxidative [5+2] cycloaddition of malonyl peroxide and double bond [6a, 7] as an alternative strategy to double bond oxidation (Scheme 1).

The present study reported new oxidative transformations of enol ethers. Malonyl peroxides react with enol ethers without transfer of solely active oxygen and formation of oxygenated products. Surprisingly, that silyl enol ethers form α-acyloxyketones with free carboxylic acid group, while methyl enol ethers yield α'-acyloxyenol ethers with free carboxylic acid group in acidic conditions. It should be noted that the starting malonyl peroxides

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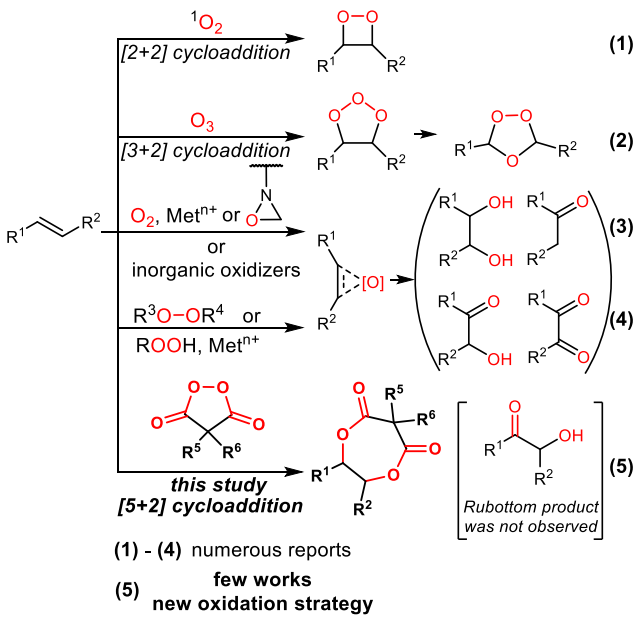
are easily synthesized in one step from available malonic acids or esters using urea hydrogen peroxide and methanesulfonic acid with good yields.[6a, 25]



Scheme 1. Diversity of double bond oxidation approaches.

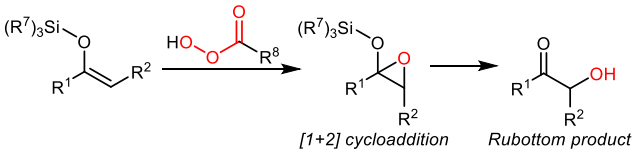
The α-oxygenated mono-carbonyl compounds are structural units in a wide range of natural and bioactive products[26] and useful intermediates for preparation of a variety of pharmaceutically active compounds.[27] Well-known examples include cortisol,[28] prednisolone,[29] paeonilactone B,[30] doxorubicin,[31] phyllaemblic acid,[32] aryloxindole,[33] donaxaridine[34] and doxycycline.[35] Hence, user-friendly methods for synthesis of α-hydroxy and α-oxo carbonyl compounds from ketones attract great attention.

In a number of studies direct hydroxylation of ketones[36] was achieved by using hypervalent iodine compounds,[37] molecular oxygen,[38] I_2/O_2,[39] DMSO/I_2 or DMSO/NBS,[40] DMSO/$CuBr_2$ or DMSO/HBr,[41] thallium(III) / *p*-nitrobenzenesulfonate,[42] $Ti(O^iPr)_4$/TBHP[43] and PhNO/TFA[44]. In regard to the oxyfunctionalization of carbonyl targets,[45] they were previously limited to the alkoxy,[46] peroxy,[47] oxygen-sulfonyl,[48] oxygen-phosphoryl,[49] aminoxy[50] groups. In a few studies α-acyloxy-carbonyl products were synthesized using Cu/CuI/air,[51] $Cu(acac)_2$/TBHP,[52] CuI/O_2,[53] Pybox–Cu(II) complex / $K_4[Fe(CN)_6]$,[54] TBAI/H_2O_2[55] or TBAI/TBHP,[56] hypervalent iodine compounds,[57] *N*-methyl-*O*-benzoylhydroxylamine hydrochloride,[58] or TBAI / electric current.[59] Apart from these reports, α-oxygenation of mono-carbonyl compounds were achieved by hydroxylation[60] and alkoxylation[61] of silyl enol ethers, hydroxylation[62] and alkoxylation[61c, 63] of alkyl enol ethers or enolates.[64] All these processes of oxyfunctionalization require addition of an external oxidant into the reaction, which usually plays oxygen-atom transfer role, as well as the removal of oxidant residual and catalysts after the reaction. To our knowledge α-oxyfunctionalization of ketones with introduction of more functionally rich fragment has not previously been accomplished.

The present study advances two aspects of modern synthetic chemistry: the use of peroxides for the development of oxidative processes and the selective oxidative C-O coupling of carbonyl compounds.

Results and Discussion

In the present work we discovered unusual chemical behavior of the malonyl peroxides with silyl and alkyl enol ethers. According to Rubottom process, acyl hydroperoxides (peracids) as a rule react with silyl enol ethers *via* [1+2] cycloaddition followed by rearrangement with formation of α-hydroxy ketones (Scheme 2).[65]



Scheme 2. Rubottom oxidation by acyl hydroperoxides.

Despite the possibility of the traditional Rubottom hydroxylation of enol ethers by peroxides,[65-66] the oxidative C-O coupling of malonyl peroxides with enol ethers selectively proceeds instead in the proposed conditions. Interestingly, the result of reaction greatly depends on the nature of enol ether – the interaction of malonyl peroxides **4** with silyl enol ethers **2** led to α-acyloxylated ketones **5**, whereas reaction of malonyl peroxides **4** with methyl enol ethers **3** affords α'-acyloxylated methyl enol ethers **6** (Scheme 3). At first glance, it seems impossible to preserve the enol double bond in the oxidative process. Two related processes are known. First, the oxidation of enol ethers by dimethyl peroxydicarbonate resulted in the introduction of methylcarbonate group in α-position.[67] Second, the reaction of lithium enolates and enol ethers with dibenzyl peroxydicarbonate forms α-benzyloxycarbonyl ketones.[68] It should be noted that the presented method makes the α-oxygenated ketones with the pendant carboxylic-acid functionality in the α-acyloxy substituent.

To get a deeper insight into the oxidative C-O coupling of malonyl peroxides with silyl enol ethers, we investigated the α-acyloxylation of acetophenone derived silyl enol ether **2a** using cyclopropyl malonyl peroxide **4a** both as the oxidant and the O-component (Table 1). To obtain product **5aa** with maximum yields, the reaction mixture was treated by NH_4Cl aqueous solution after the reaction was complete.

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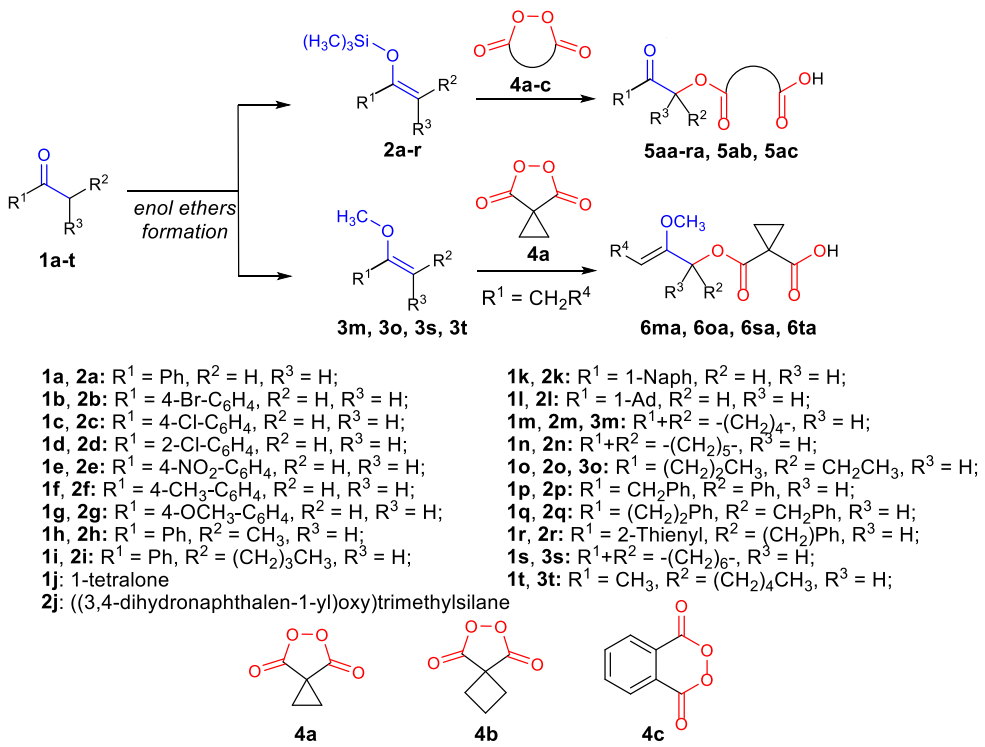
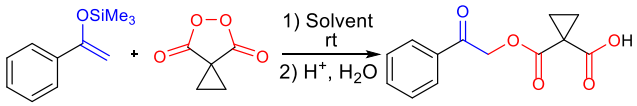


Scheme 3. Preparation of silyl enol ethers **2a-r** and methyl enol ethers **3m**, **3o**, **3s**, **3t** from ketones **1a-t**. Synthesis of α-acyloxyketones **5aa-ra**, **5ab**, **5ac** from silyl enol ethers **2a-r** and peroxides **4a-c** and α'-acyloxyenol ethers **6ma**, **6oa**, **6sa**, **6ta** from methyl enol ethers **3m**, **3o**, **3s**, **3t** and malonyl peroxide **4a**.

Table 1. Optimization of the oxidative C-O coupling of cyclopropyl malonyl peroxide **4a** with silyl enol ether **2a**.[a)]



2a **4a** **5aa**

Entry	Solvent	Time, h	Yield **5aa**, %
1	CH_2Cl_2	5	43
2	CH_2Cl_2	24	46
3	CH_3CN	5	45
4	Et_2O	5	53
5	THF	5	68
6	THF	24	70
7 [b)]	THF	5	92
8 [b)]	1,4-dioxane	5	89
9 [b)]	EtOAc	5	85
10 [b)]	acetone	5	58
11 [b)]	$CHCl_3$	5	53
12 [b), c)]	-	2	30

[a)] **General procedure**: Cyclopropyl malonyl peroxide **4a** (1.2 mmol, 153.6 mg) was added to a solution of **2a** (1.0 mmol, 192.3 mg) in a solvent (2 mL). Reaction mixture was stirred for 5 or 12 h at 20-25 °C then treated by NH_4Cl aq. solution. [b)] 1.5 mmol (192.2 mg) cyclopropyl malonyl peroxide **4a**. [c)] reaction without solvent at 90 °C, for 2 h.

Firstly, silyl enol ether **2a** was converted into C-O coupling product **5aa** in CH_2Cl_2 as a solvent (Table 1, entries 1-2). However, there was only 43% yield of **5aa** within 5 h, which did not significantly increase with time (24 h, 46%, entry 2). When the reaction was performed in CH_3CN, Et_2O, THF for 5 h (entries 3-5) the best result was achieved in THF (68 %, entry 5). The increase of the reaction time to 24 h did not lead to a significant increase in yield (entry 6). The 85-92 % yields of **5aa** were achieved with 1.5 eq. of malonyl peroxide **4a** and THF, dioxane or EtOAc as a solvent for 5 h (entries 7-9). Acetone and $CHCl_3$ resulted **5aa** in 58 % and 53 % yields (entries 10 and 11). The attempt to improve the yield of **5aa** performing the reaction without a solvent led to poor result (entry 12). The main by-product in entries 1-11 was starting acetophenone **1a** as a result of **2a** hydrolysis.

With the optimized conditions in hand (Table 1, entry 7), we next explored the substrate scope to demonstrate the generality of the α-acyloxylated ketones **5** synthesis *via* the oxidative C-O coupling of malonyl peroxides **4** with silyl enol ethers **2**. To improve the procedure, we decided to perform the whole sequence of ketones **1** transformations into the final products without the time-consuming isolation and purification of enol ethers.[69] For this purpose, the ketones **1** were silylated using a chlorosilane/NaI/NEt_3 combination,[70] and crude silyl enol ethers **2** produced in virtually quantitative yields,

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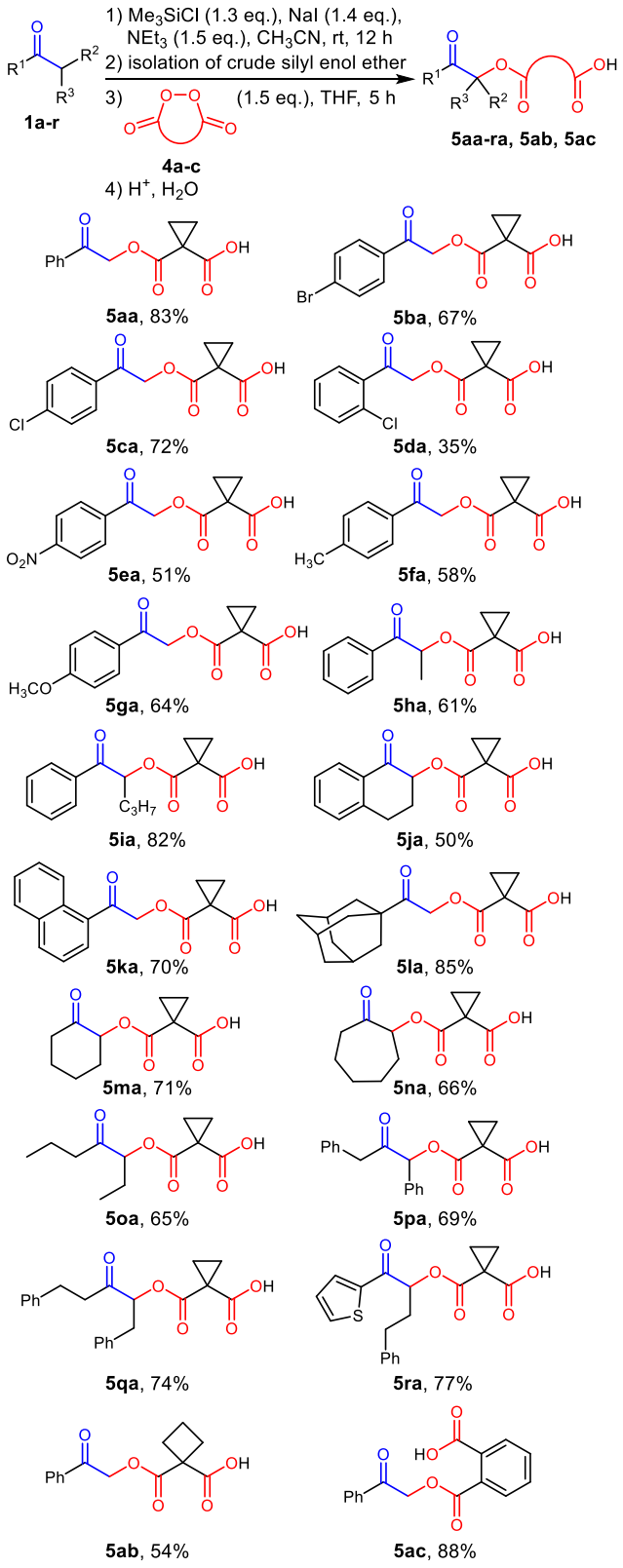
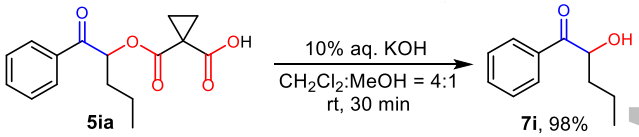
were subjected to further reactions with malonyl peroxides **4** without purification (Scheme 4).



Scheme 4. Synthesis of α-acyloxylated ketones **5** from ketones **1**. Reaction conditions: 1) ketone **1** (98.2-238.3 mg, 1.0 mmol, 1.0 eq.), NaI (210 mg, 1.4 mmol, 1.4 eq.), Et_3N (152 mg, 1.5 mmol, 1.5 eq.), Me_3SiCl (165.0 µL, 141.2 mg, 1.3 mmol, 1.3 eq.), CH_3CN (1 mL), 12 h, 0 °C → 20-25 °C. 2) isolation of crude silyl enol ether. 3) peroxide **4** (1.5 mmol, 192.2-363.3 mg), THF (2 mL), 5 h, 0 °C → 20-25 °C. 4) treatment by NH_4Cl aq. solution. Isolated yield of **5aa-ra**, **5ab**, **5ac** based on ketone **1a-r**.

The α-acyloxylated aryl ketones **5aa-ka** were obtained in 50% (for **5ja**) to 83% (for **5aa**) yields excepting the product **5da** prepared from 2-chloroacetophenone **1d** (35%). The influence of electron-donating or electron-withdrawing substituents on the products **5aa-ka** yields was not observed. The products **5la-oa** from the aliphatic ketones **1l-o** were prepared in 65-85 % yields. Presence of benzylic or thienyl group increases the yields of α-acyloxylated ketones, the products **5pa-ra** were obtained in 69-77% yields. The flexibility of this approach in selection of starting materials is illustrated by facile formation of the product **5ra** from easily oxidizable thiophene-containing ketone **1r**. Phthaloyl peroxide **4c** resulted in α-acyloxy ketone **5ac** with 88 % yield.

We further examined the possibility of smooth hydrolysis of the C-O coupling product **5ia** with formation of the α-hydroxy ketone **7i** and found that the malonate derivative **5ia** can be easily transformed into **7i** with 98 % yield (Scheme 5).



Scheme 5. Hydrolysis of the product **5ia** to form the α-hydroxy ketone **7i**.

The reaction of cyclopropyl malonyl peroxide **4a** with methyl enol ethers **3m** in optimized conditions (Table 1, entry 7) did not lead to product **5ma**. Instead, unexpected cyclic oxidative C-O coupling product **8ma** was detected in the reaction mixture by NMR (see SI). After exclusion of "treatment by NH_4Cl aq. solution" step and a slight changes in the conditions of coupling of cyclopropyl malonyl peroxide **4a** with methyl enol ethers **3m**, we were able to isolate the cyclic product **8ma** in individual state with 15% yield (Scheme 6). The second product in the reaction was truly remarkable - unstable compound **6ma** containing both carboxylic acid and enol fragment was isolated with 9% yield. It was shown that cyclic product **8ma** rearranges into **6ma** in acidic conditions (Scheme 6).

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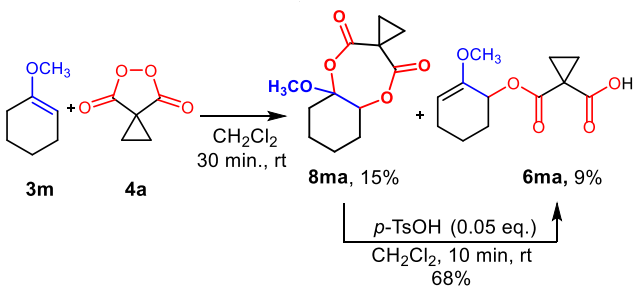
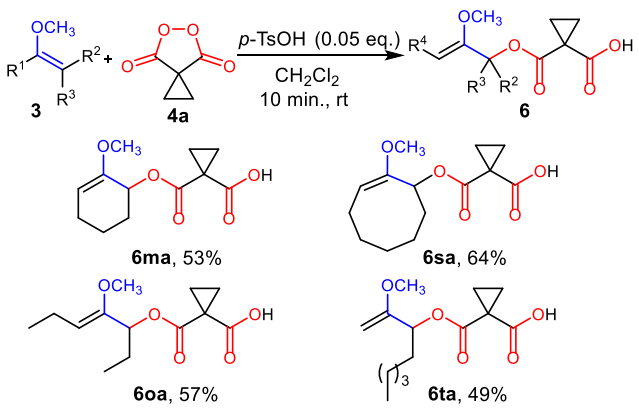


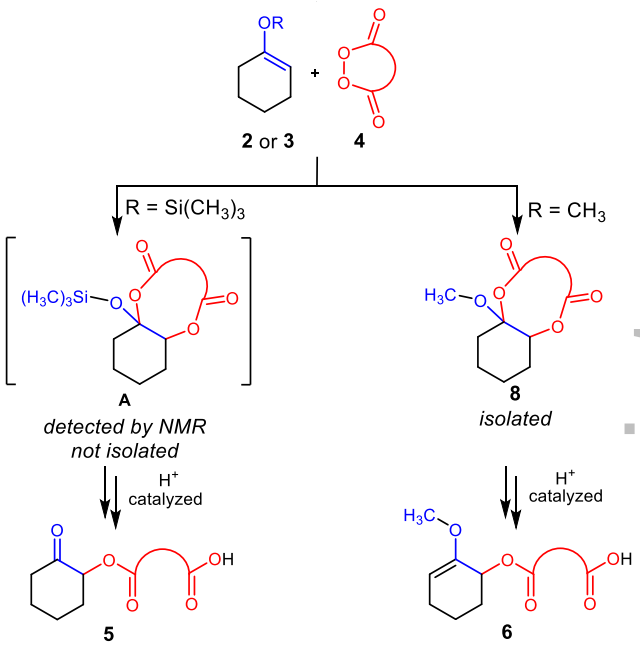
Scheme 6. Oxidative C-O coupling of malonyl peroxide **4a** with methyl enol ether **3ma** with the formation of unexpected products **8ma** and **6ma**.

When we carried out TsOH-catalyzed reaction of malonyl peroxide **4a** with methyl enol ethers **3**, we were surprised to observe selective unusual oxidative transformation – oxidative C-O coupling with retaining of easily oxidizable enol fragment (Scheme 7). The liable C-O coupling products **6** containing both carboxylic acid and enol fragment were synthesized from cyclopropyl malonyl peroxide **4a** and methyl enol ethers **3** with 49-64% yields (Scheme 7).



Scheme 7. Oxidative C-O coupling of malonyl peroxide **4a** with methyl enol ethers **3** with retaining of enol fragment.

Suggesting a mechanism, we believe that the reaction proceeds as outlined in Scheme 8. The nucleophilic attack by the double bond of the enol ether **2** or **3** on a weak peroxide bond[71] resulted in unstable cyclic acetal **A** (detected by NMR in $CDCl_3$ solution, see SI) in the case of silyl enol ethers **2** or isolable cyclic acetal **8**[6a, 7] in the case of methyl enol ethers **3**. The unstable cyclic acetal **A** could not be isolated in pure form even though formation of acetals from peroxides is general favorable due to greater strength of the C-O vs. O-O bond and stabilization by the anomeric effect.[72] Hydrolysis of **A** results in the α-acyloxy ketones **5**. In acidic conditions[3] cyclic acetal **A** is transformed into the α-acyloxy ketones **5** (see SI) with abstraction of trimethylsilyl group as $Si(CH_3)_3$ cation elimination is more favorable than deprotonation.[73] In the case of methyl enol ethers **3** acid-catalyzed rearrangement of the intermediate **8** yields the α-acyloxy enol ethers **6** (see Scheme 6).



Scheme 8. Proposed reaction mechanism of C-O coupling products formation.

This mechanistic pathway is consistent with previous investigations of the reactivity of the malonyl peroxides **4**.[6b, 6e] Based on the obtained results we can consider the discovered oxidative C-O coupling of malonyl peroxides with enol ethers as oxidative [5+2] cycloaddition from the formal point of view.

Conclusion

In summary, we disclosed oxidative C-O coupling of malonyl peroxides with enol ethers proceeding *via* oxidative [5+2] cycloaddition. Traditional Rubottom oxidation of enol ethers with the formation of solely active oxygen atom transfer products was not observed. From the silyl enol ethers, the α-acyloxy ketones were prepared with 35-88 % yields. In the case of methyl enol ethers unusual oxidative transformation was observed – oxidative C-O coupling with retaining of easily oxidizable enol fragment. The paradoxical situation of saving of enol double bond in the oxidative process illustrates the unlimited possibilities of malonyl peroxides in organic synthesis. Convenient *one-pot* method for the preparation of the α-acyloxyketones with a free carboxylic acid group from ketones with yields 35-88% on two steps *via* silyl enol ethers formation and oxidation was developed.

Experimental Section

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Experimental Procedures for Table 1.

Experimental Procedure for Table 1, entries 1-11.

Cyclopropyl malonyl peroxide **4a** (1.2-1.5 mmol, 153.6-192.2 mg, 1.2-1.5 eq.) was added to a solution of **2a** (1.0 mmol, 192.3 mg, 1.0 eq.) in CH_2Cl_2, CH_3CN, Et_2O, THF, 1,4-dioxane, EtOAc, acetone, $CHCl_3$ (2 mL) at 0-5 °C. The reaction mixture was stirred for 5 or 24 h at 20-25 °C. Later, saturated aqueous NH_4Cl (10 mL) was added, the mixture was extracted with CH_2Cl_2 (3×15 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20–25 °C). Product **5aa** was isolated by column chromatography on SiO_2 (CH_2Cl_2:EtOAc = from 15:1 to 5:1).

Experimental Procedure for Table 1, entry 12.

Cyclopropyl malonyl peroxide **4a** (1.5 mmol, 192.2 mg, 1.5 eq.) was added to **2a** (1.0 mmol, 192.3 mg, 1.0 eq.) at 0-5 °C. The reaction mixture was stirred for 2h at 90 °C. After cooling to room temperature saturated aqueous NH_4Cl (10 mL) was added, the mixture was extracted with CH_2Cl_2 (3×15 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20–25 °C). Product **5aa** was isolated as described above.

Experimental Procedure for Scheme 4.

*Preparation of silyl enol ethers **2**.*[70]

NaI (1.4 mmol, 210.0 mg, 1.4 eq.) was placed in a round bottom flask and dried under vacuum (15-20 mmHg) using a heat gun (gun temperature 100-150 °C) for 5 min. After cooling to room temperature, the flask was filled with argon. Then, CH_3CN (1 mL), ketone **1** (1.0 mmol, 1.0 eq.), and Et_3N (1.5 mmol, 151.8 mg, 1.5 eq.) were successively added. The mixture was cooled with an ice/water bath, and Me_3SiCl (1.3 mmol, 141.2 mg, 165.0 μL, 1.3 eq.) was added at 0 °C. The cooling bath was removed, and the mixture was stirred for 12 h at room temperature. Then, volatile components were evaporated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 40–45 °C). The solid residue was washed with hexane (3×15 mL) (the hexane layers were decanted and filtered through a cotton plug). The combined filtrates were concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20–25 °C), furnishing the silyl enol ether **2** which was used without purification.

*C-O coupling of malonyl peroxides **4** with silyl enol ethers **2**.*

Peroxide **4** (1.5 mmol, 192.2-363.3 mg, 1.5 eq.) was added to a solution of crude silyl enol ether **2** in dry THF (2 mL) at 0-5 °C. The reaction mixture was stirred 5 h at 20-25 °C. Later, saturated aqueous NH_4Cl (10 mL) was added, the mixture was extracted with CH_2Cl_2 (3×15 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20–25 °C). Products **5aa-ra, 5ab** were isolated by column chromatography on SiO_2 (CH_2Cl_2:EtOAc = from 30:1 to 5:1). Product **5ac** was isolated by recrystallization from EtOH.

Experimental Procedure for Scheme 5.[74]

10% aq. KOH (5 mL) was added to a solution of C-O coupling product **5ia** (1.0 mmol, 290.3 mg) in CH_2Cl_2:MeOH = 4:1 (20 mL). The reaction was stirred at 20-25 °C for 30 min. Later, the mixture was diluted with EtOAc (100 mL), washed with water (3×10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure using a rotary evaporator (15-20 mmHg), (bath temperature, ca. 20–25 °C). The product **7i** was isolated by column chromatography on SiO_2 (PE:EtOAc = from 20:1 to 2:1).

Experimental Procedures for Scheme 6.

Methyl enol ether **3ma** (1.0 mmol, 112.2 mg, 1.0 eq.) was added to a solution of malonyl peroxide **4a** (1.0 mmol, 128.1 mg, 1.0 eq.) in CH_2Cl_2 (2 mL) at 0-5 °C. The reaction mixture was stirred 30 min. at 20-25 °C. After that the reaction mixture was transferred onto SiO_2 chromatographic column and products **8ma** and **6ma** were isolated with use of mixture PE:EtOAc (7:1) as eluent.

*TsOH-catalyzed rearrangement of **8ma** into **6ma**.*

p-TsOH·H_2O (0.01 mmol, 1.9 mg, 0.05 eq.) was added to a solution of **8ma** (0.2 mmol, 48.1 mg, 1.0 eq) in CH_2Cl_2 (2 mL). The reaction mixture was stirred 10 min. at 20-25 °C. After that the reaction mixture was transferred onto SiO_2 chromatographic column and product **6ma** (68%, 32.7 mg, 0.14 mmol) was isolated with use of mixture PE:EtOAc (7:1) as eluent.

Experimental Procedure for Scheme 7.

p-TsOH·H_2O (0.05 mmol, 9.5 mg, 0.05 eq.) was added to a solution of malonyl peroxide **4a** (1.1 mmol, 141.0 mg, 1.1 eq.) in CH_2Cl_2 (2 mL). Later, methyl enol ether **3** (1.0 mmol, 112.2-142.2 mg, 1.0 eq.) was added dropwise with stirring at 0-5 °C. The reaction mixture was stirred for 10 min. at 20-25 °C. After that the reaction mixture was transferred onto SiO_2 chromatographic column and the product **6** was isolated with the use of mixture PE:EtOAc (7:1) as eluent.

Acknowledgements

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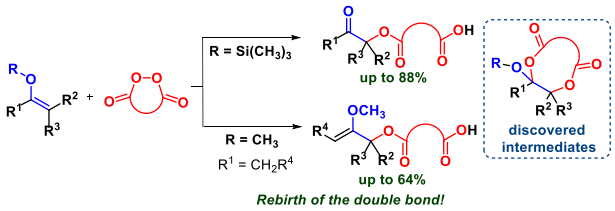

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