

Pentafluoroperbenzoic acid as the efficient reagent for Baeyer–Villiger oxidation of cyclic ketones

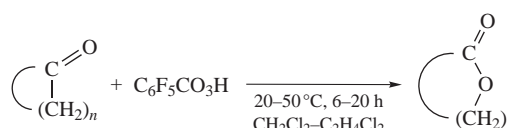
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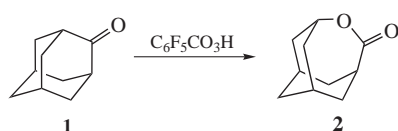
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The Baeyer–Villiger oxidation of cyclic ketones with pentafluoroperbenzoic acid provides the corresponding lactones in 40–98% yields.



The oxidation of cyclic ketones with molecular oxygen,^{1,2} hydrogen peroxide,^{3–6} or peracids,^{7–10} is an efficient access to lactones. In this work, we report the Baeyer–Villiger oxidation of cyclic ketones using pentafluoroperbenzoic acid (PFPBA), which has been already employed in the organic synthesis, *e.g.*, for the epoxidation of olefins^{11,12} and hydroxylation of adamantanes.^{13,14} PFPBA is stable: its thermal decomposition begins at 93 °C according to the derivatographic analysis, it remains stable during storage (*e.g.*, the loss of active oxygen at 20 °C does not exceed 1.5% after 2 months), and it is shock-resistant as compared to *m*-chloroperbenzoic acid (*m*CPBA).¹⁵ Taking into account the high reactivity of PFPBA, we believed that it could serve as an active and selective oxidizer of cyclic ketones.

Adamantan-2-one **1** was chosen as the model example to optimize the conditions for the Baeyer–Villiger oxidation with PFPBA. The reaction employing 1:1 reagent ratio at room temperature for 6 h provided 4-oxahomoadamantan-5-one **2** in 40% yield (Scheme 1, Table 1, entry 1). An introduction of oxo-



Scheme 1 Conditions: CH₂Cl₂–C₂H₄Cl₂, 20 °C, 6 h.

Table 1 The influence of PFPBA concentration, catalyst MoO(O₂)₂·2QOH, and reaction conditions on the yield of lactone **2**.^a

Entry	1:PFPBA ratio	[Mo] (mol%)	Yield of 2 (%)
1	1:1	–	40
2	1:1	1	33
3	1:1	3	50
4	1:1	5	54
5	1:1.2	–	76
6	1:1.2	5	78
7 ^b	1:1.5	–	82
8 ^c	1:1.5	–	84
9	1:1.5	–	98
10 ^d	1:1.5	–	57
11 ^d	1:1.5	5	62

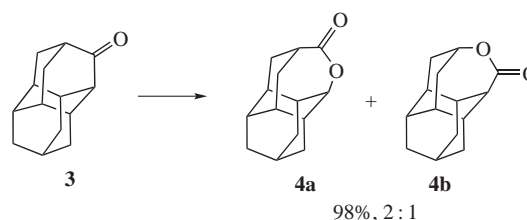
^aReaction conditions: 20 °C, 6 h. ^bThe duration of reaction is 1 h. ^cThe duration of reaction is 3 h. ^dThe oxidizer is *m*CPBA.

peroxy complex of molybdenum MoO(O₂)₂·2QOH (QOH is 8-hydroxyquinoline) as the catalyst (5 mol%) insignificantly increased the yield of lactone **2** (to 54%, see Table 1, entry 4). When the PFPBA amount was raised to 1.5 equiv., the yield of lactone **2** rose to 98% in the absence of the catalyst (entry 9).[†]

To evaluate the relative activity of PFPBA in comparison with other oxidizers, experiments on the oxidation of adamantan-2-one **1** with *m*CPBA were carried out. Under the similar conditions (20 °C, 6 h, without or with [Mo]), product **2** was formed in yields of 57 or 62% (see Table 1, entries 10 and 11). Thus, PFPBA is a stronger oxidizing agent than *m*CPBA.

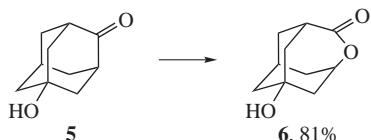
Diamantanone **3** also reacts smoothly with PFPBA under the similar conditions (20 °C, 6 h) and provides a 2:1 mixture of 11-oxahomodiamantan-10-one **4a** and 10-oxahomodiamantan-11-one **4b** (Scheme 2). The ratio between lactones **4a** and **4b** was determined from the comparison of ¹H and ¹³C NMR spectra with the previously reported data, when the similar mixture of lactones (**4a**:**4b** = 1.7:1) was obtained *via* oxidation of **3** with a fivefold excess of peracetic acid at 40 °C.

Oxidation of 5-hydroxyadamantan-2-one **5** proceeded with incomplete conversion (67%) at 20 °C after 6 h to give 1-hydroxy-4-oxahomoadamantan-5-one **6**. The introduction of [Mo] catalyst



Scheme 2 Reagents and conditions: C₆F₅CO₃H (1.5 equiv.), CH₂Cl₂–C₂H₄Cl₂, 20 °C, 6 h.

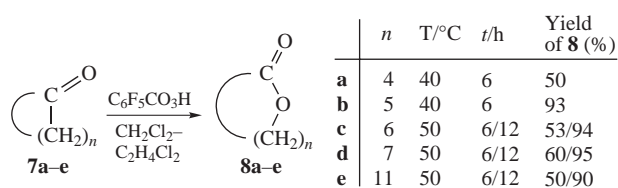
[†] A solution of PFPBA (0.68 mmol) in CH₂Cl₂ (2 ml) was added dropwise to the solution of adamantan-2-one **1** (0.05 g, 0.33 mmol) in dichloroethane (2 ml) at 20 °C for 1 h, and the reaction mixture was stirred for additional 5 h. Once the reaction was finished, aqueous Na₂CO₃ (10%) was added, and the mixture was stirred for 5 min. The organic layer was filtered through Al₂O₃ (CH₂Cl₂–dichloroethane as the eluent), while the aqueous one was extracted with CHCl₃. The organic fractions were combined and the solvent was evaporated. The reaction products were isolated by column chromatography on silica gel (60–200 μm, 60 Å) using ethyl acetate as the eluent.



Scheme 3 Reagents and conditions: $\text{C}_6\text{F}_5\text{CO}_3\text{H}$ (1.5 equiv.), $\text{MoO}(\text{O}_2)_2 \cdot 2\text{QOH}$ (5 mol%), CH_2Cl_2 – $\text{C}_2\text{H}_4\text{Cl}_2$, 20 °C, 6 h.

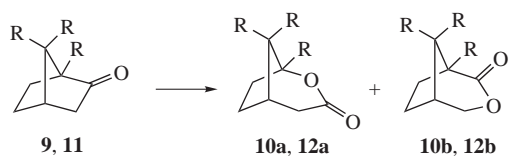
allowed us to increase the yield of lactone **6** up to 81% at the full conversion of **5** (Scheme 3).

To estimate the PFPBA opportunities as the versatile oxidizer, cycloalkanones C_5 – C_8 and C_{12} **7a–e** were tested. The reaction was processed at the twofold excess of PFPBA providing the corresponding lactones **8a–e** (Scheme 4). High yields of lactones **8c–e** were achieved under the conditions of 50 °C and 12 h. In the oxidation of cyclopentanone **7a**, the yield of 5-pentanolide **8a** did not exceed 50% due to the formation of side 5-hydroxypentanoic acid. Note that to achieve high yields of lactones **8a–e** using *m*CPBA, a prolonged exposure at 20 °C for 5 days¹⁷ and 70 °C for 7 days¹⁸ is required.



Scheme 4

Oxidation of norbornan-2-one **9** at 20 °C in the presence of [Mo] catalyst gives single regioisomer **10a** of two possible (Scheme 5). The highest yield of lactone **10a** (94%) was achieved in the presence of 5 mol% of the catalyst, while in the absence of the catalyst it was 67%. The analogous oxidation with *m*CPBA is non-selective and affords a mixture of isomeric lactones **10a,b**.¹⁹ The oxidation of camphor **11** required a prolonged heating (40 °C, 20 h) in the presence of twofold amount of PFPBA, providing a mixture of regioisomeric campholides **12a,b** in the total yield of 40% (see Scheme 5). The first experiment on the oxidation of camphor **11** with PFPBA was carried out at a lower



	R	$\text{C}_6\text{F}_5\text{CO}_3\text{H}$ (equiv.)	[Mo] (mol%)	Solvent	T/°C	<i>t</i> /h	Products	Yield (%)
9	H	1.5	5	CH_2Cl_2 – $\text{C}_2\text{H}_4\text{Cl}_2$	20	6	10a	94
11	Me	2	–	CH_2Cl_2	40	20	12a + 12b (1 : 2.5)	Σ40

Scheme 5

temperature (20 °C, 30 days), which could explain the low yield (27%) of lactones **12a,b**.¹⁴

In summary, we have demonstrated that pentafluoroperbenzoic acid is a promising and efficient Baeyer–Villiger reagent highly competitive with traditional *m*CPBA.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.11.027.

References

- X.-T. Zhou, H.-B. Ji and Q.-L. Yuan, *J. Porphyrins Phthalocyanines*, 2008, **12**, 94.
- S. Chen, X. Zhou, Y. Li, R. Luo and H. Ji, *Chem. Eng. J.*, 2014, **241**, 138.
- X. Hao, O. Yamazaki, A. Yoshida and J. Nishikido, *Tetrahedron Lett.*, 2003, **44**, 4977.
- X. Hao, O. Yamazaki, A. Yoshida and J. Nishikido, *Green Chem.*, 2003, **5**, 524.
- M. Uyanik, D. Nakashima and K. Ishihara, *Angew. Chem. Int. Ed.*, 2012, **51**, 9093.
- V. A. Vil', G. dos Passos Gomes, O. V. Bityukov, K. A. Lyssenko, G. I. Nikishin, I. V. Alabugin and A. O. Terent'ev, *Angew. Chem. Int. Ed.*, 2018, **57**, 3372.
- R. R. Sauers, *J. Am. Chem. Soc.*, 1959, **81**, 925.
- T. Muller, D. Coowar, M. Hanbali, P. Heuschling and B. Luu, *Tetrahedron*, 2006, **62**, 12025.
- J. P. Genet and P. Kahn, *Tetrahedron Lett.*, 1980, **21**, 1521.
- I. A. Yaremenko, V. A. Vil', D. V. Demchuk and A. O. Terent'ev, *Beilstein J. Org. Chem.*, 2016, **12**, 1647.
- U. M. Dzhemilev, N. S. Vostrikov, A. M. Moiseenkov and G. A. Tolstikov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28**, 857 (*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 913).
- U. M. Dzhemilev, N. S. Vostrikov, A. M. Moiseenkov and G. A. Tolstikov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 1051 (*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1320).
- R. I. Khusnutdinov and T. M. Oshnyakova, *Russ. J. Org. Chem.*, 2015, **51**, 123 (*Zh. Org. Khim.*, 2015, **51**, 125).
- R. I. Khusnutdinov, T. M. Oshnyakova, L. M. Khalilov, A. R. Baibuldina and U. M. Dzhemilev, *Russ. J. Org. Chem.*, 2016, **52**, 1121 (*Zh. Org. Khim.*, 2016, **52**, 1131).
- U. M. Dzhemilev, N. S. Vostrikov, G. A. Tolstikov and S. R. Rafikov, *USSR Author's Certificate 807610*, 1980.
- J. Ondráček, J. Janků, J. Novotný, L. Vodička, L. Csordás and B. Kratochvíl, *Collect. Czech. Chem. Commun.*, 1989, **54**, 3260.
- R. Randino, E. Cini, A. M. D'Ursi, E. Novellino and M. Rodriguez, *Tetrahedron Lett.*, 2015, **56**, 5723.
- J. A. Wilson, S. A. Hopkins, P. M. Wrigh and A. P. Dove, *Macromolecules*, 2015, **48**, 950.
- P. Hamley, A. B. Holmes, D. R. Marshall and J. W. M. MacKinnon, *J. Chem. Soc., Perkin Trans. 1*, 1991, 1793.

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