

meta-Chloroperoxybenzoic Acid (*m*-CPBA)

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Anton Merkushev was born in Perm, Russian Federation, in 1989. He obtained his B.Sc. (2011) and M.Sc. (2013) in organic chemistry at Perm State University, Perm. Currently, he is working towards his Ph.D. in the Institute of Technical Chemistry UB RAS under the supervision of Professor Dr. Alexander Butin. His research interests are focused on oxidative transformations of furan substrates.



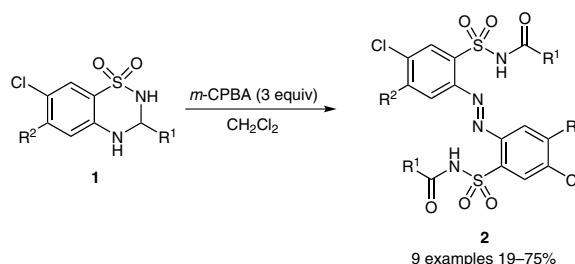
Introduction

meta-Chloroperoxybenzoic acid (*m*-CPBA) is a white crystalline powder with a melting point of 90 °C. In pure form, it can be detonated by shock or by sparks, and therefore it is stored as a mixture containing less than 72% *m*-CPBA (containing water and *meta*-chlorobenzoic acid). It is soluble in dichloromethane, chloroform, ethyl acetate, alcohol, and

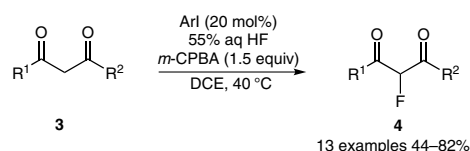
insoluble in hexanes, carbon tetrachloride, and water. *m*-CPBA is obtained by the reaction of *m*-chlorobenzoyl chloride with a basic solution of hydrogen peroxide in the presence of MgSO₄·7H₂O. *m*-CPBA is used as oxidizing agent in Baeyer–Villiger oxidations¹ and in the synthesis of epoxides,² oxaziridines,³ α-disulfines,⁴ sulfoxides and sulfones,⁵ N-oxides,⁶ and ketones.⁷

Table 1 Use of *m*-CPBA

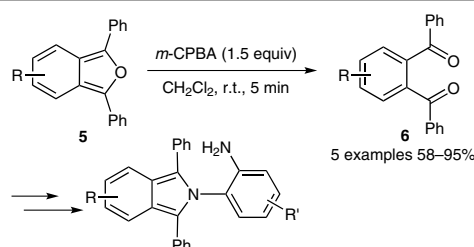
(A) Troisi and co-workers developed a new synthetic pathway to sulfonamidic azobenzene derivatives **2** based on the oxidation of 2,3-dihydrobenzothiadiazines **1** with *m*-CPBA. It was shown that high yields were achieved when three equivalents of the peroxyacid were used.⁸



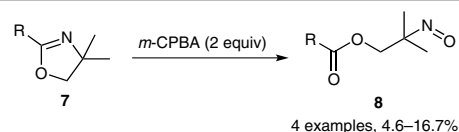
(B) Recently, Kitamura et al. found that oxidative fluorination of 1,3-dicarbonyl compounds **3** with hydrofluoric acid is efficiently performed with the use of stoichiometric amounts of *m*-CPBA. It is worth noting that a catalytic amount of iodoarene is needed for the reaction to proceed.⁹



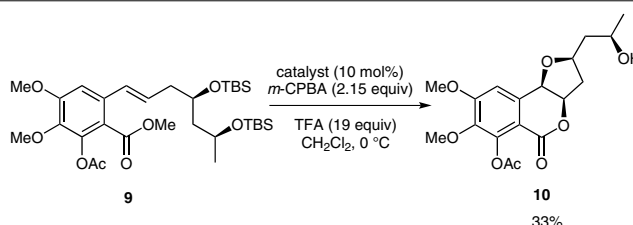
(C) Bovenkerk and Esser showed that the oxidation of different benzo[c]furans **5** with *m*-CPBA afforded diketones **6**, that were used as precursors for 2-aniline-substituted isoindoles.¹⁰



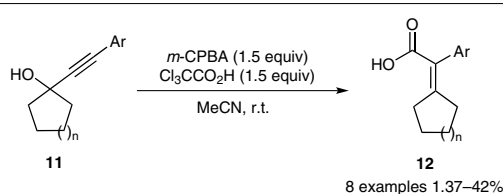
(D) Nitroso esters **8**, which are attractive monomers for synthesis of different polymers with high molecular weight and regular monomer sequence, were obtained by the reaction of 4,4-dimethyl-2-oxazolines **7** with two equivalents of *m*-CPBA. Monomers with a similar structure may be obtained when 4,4-dimethyl dihydro-1,3-oxazines are used as starting materials.¹¹



(E) The double oxylactonization of **9** in the presence of *m*-CPBA and dimethyl 2,2'-((2-iodo-1,3-phenylene)bis(oxy))(2*S*,2'*S*)-dipropionate as a catalyst was a key step in total synthesis of a monocerin derivative **10**, a potentially biologically active compound. The stereochemistry is controlled by an iodoarene catalyst.¹²



(F) Rodríguez and Moran studied an interesting oxidative rearrangement of tertiary propargylic alcohols **11** to enoic acids **12** in the presence of *m*-CPBA. They suggested that the reaction proceeds by hydrogen-bond directed alkyne epoxidation followed by 1,2-aryl migration.¹³



Acknowledgement

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References

- (1) Zhang, Z. G.; Roiban, G. D.; Acevedo, J. P.; Polyak, I.; Reetz, M. T. *Adv. Synth. Catal.* **2013**, 355, 99.
- (2) Huang, A. C.; Sumby, C. J.; Tiekink, E. R. T.; Taylor, D. K. *J. Nat. Prod.* **2014**, 77, 2522.
- (3) (a) Perrone, S.; Rosato, F.; Salomone, A.; Troisi, L. *Tetrahedron* **2013**, 69, 3878. (b) Carroccia, L.; Fioravanti, S.; Pellacani, L.; Sadun, C.; Tardella, P. A. *Tetrahedron* **2011**, 67, 5375.
- (4) Okuma, K.; Munakata, K.; Tsubota, T.; Kanto, M.; Nagahora, N.; Shioji, K.; Yokomori, Y. *Tetrahedron* **2012**, 68, 6211.
- (5) Džambaski, Z.; Marković, R.; Kleinpeter, E.; Baranac-Stojanović, M. *Tetrahedron* **2013**, 69, 6436.
- (6) Zheng, J.; You, S. L. *Chem. Commun.* **2014**, 50, 8204.
- (7) Deng, J. C.; Chuang, S. C. *Org. Lett.* **2014**, 16, 5792.
- (8) Cannazza, G.; Perrone, S.; Rosato, F.; D'Accolti, L.; Parenti, C.; Troisi, L. *Synthesis* **2014**, 46, 962.
- (9) Kitamura, T.; Muta, K.; Kuriki, S. *Tetrahedron Lett.* **2013**, 54, 6118.
- (10) Bovenkerk, M.; Esser, B. *Eur. J. Org. Chem.* **2015**, 775.
- (11) Li, J.; Wang, Q. *J. Polym. Sci. Polym. Chem.* **2014**, 52, 810.
- (12) Fujita, M.; Mori, K.; Shimogaki, M.; Sugimura, T. *RSC Adv.* **2013**, 3, 17717.
- (13) Rodríguez, A.; Moran, W. J. *Synlett* **2013**, 24, 102.