mun. **1991**, 1672. and references cited therein.
4. (a) D. Craig and K. Daniels, *Tetrahedron Lett.* **1990**, *31*, 6441. (b) D. Craig and K. Daniels, *Tetrahedron Lett.* **1991**, *32*, 6973.
5. To a solution of diethyl chloro(phenylthio)methanephosphonate (0.02 mol) **2** in chloroform (30 mL) was added dropwise a solution of *m*-chloroperbenzoic acid (4.2 g, 0.02 mol) in chloroform (30 mL) at 0 ℃. The mixture was stirred at 0 ℃ for 1 hr and then allowed to stand overnight at room temperature. The insoluble materials were filtered off, and the filtrate was washed with 10% aqueous sodium carbonate solution (3×10 mL), water (10 mL), and brine (10 mL), dried, filtered, and concentrated. The residue was chromatographed on silica gel using ethyl acetate : hexane = 1 : 1 to give the sulfoxide **3**. Selected data for **3**: mp 51-53 ℃. ^{1}H NMR ($CDCl_3$) δ 1.34 (m, 6H, OCH_2CH_3), 4.27 (m, 4H, OCH_2CH_3), 4.47 (d, 1H, CHCl, J_{PH} = 11.48 Hz, major diastereomer) and 4.74 (d, 1H, CHCl, J_{PH} = 10.05 Hz, minor diastereomer), 7.51-7.82 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) δ 16.18, 64.80, 70.64 (d, J_{PC} = 150.0 Hz), 124.83 (126.51), 129.04 (128.57), 131.92 (132.49), 140.84 (140.00). ^{31}P NMR ($CDCl_3$) δ 11.97 and 11.07. IR($CDCl_3$) 1274 (P=O, s), 1047 (S=O, vs) cm^{-1}. MS m/e = 65 (26.2), 93 (30.5), 125 (100), 157 (29.1), 159 (8.7), 310 (3.9, M), 312 (1.3, M+2).
6. T. H. Kim and D. Y. Oh, *Tetrahedron Lett.* **1985**, *26*, 3479.
7. Selected data for **4a**: ^{1}H NMR ($CDCl_3$) δ Z: 1.82 (d, 3H, J = 6.91 Hz), 6.76 (q, 1H), 7.38-7.60 (m, 5H), E: 2.16 (d, 3H, J = 7.48 Hz), 6.36 (q, 1H), 7.42-7.63 (m, 5H). IR($CDCl_3$) 1055 (S=O, vs) cm^{-1}.
Selected data for **4b**: ^{1}H NMR ($CDCl_3$) δ Z: 1.10 (t, 3H), 2.36 (qn, 2H), 6.80 (t, 1H, J = 7.25 Hz), 7.49-7.79 (m, 5H), E: 1.20 (t, 3H), 2.86 (dm, 2H), 6.34 (t, 1H, J = 8.10 Hz), 7.51-7.71 (m, 5H). IR($CDCl_3$) 1056 (S=O, vs) cm^{-1}.
Selected data for **4c**: ^{1}H NMR ($CDCl_3$) δ Z: 1.07 (d, 6H), 2.82 (m, 1H), 6.61 (d, 1H, J = 9.20 Hz), 7.47-7.66 (m, 5H), E: 1.11 (dd, 6H), 3.35 (m, 1H), 6.10 (d, 1H, J = 10.80 Hz), 7.45-7.60 (m, 5H). IR($CDCl_3$) 1056 (S=O, vs) cm^{-1}.
Selected data for **4d**: ^{1}H NMR ($CDCl_3$) δ Z: 1.21 (brs, 11H), 6.59 (d, 1H, J = 9.38 Hz), 7.42-7.62 (m, 5H), E: 1.67 (brs, 11H), 6.13 (d, 1H, J = 10.66 Hz), 7.38-7.60 (m, 5H). IR ($CDCl_3$) 1056 (S=O, vs) cm^{-1}.
8. Synthesis of **4** in a three steps from aldehydes, see: T. Satoh, Y. Hayashi, and K. Yamakawa, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1866.

New Method of Generating Trifluoroperoxyacetic acid for the Baeyer-Villiger Reaction

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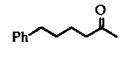
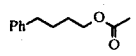
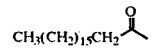
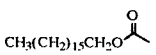
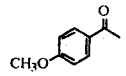
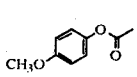
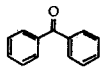
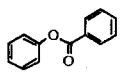
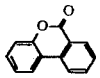
The Baeyer-Villiger oxidation of ketones to esters is of considerable synthetic use and has been performed with a variety of organic peroxy acids in those cases where the ketone is alicyclic, aralkyl or aromatic.[1] However, ketones, especially of the type RCH_2COCH_2R', do not readily undergo oxidation to the corresponding esters with conventional reagents such as perbenzoic, substituted perbenzoic, peroxyacetic, and Caro's acid. It has been reported that trifluoroperoxyacetic acid (TFPAA) has been shown to be an effective reagent for this type of reaction.[2,3] Reactions with this reagent are rapid and clean, giving high yields of product, though it is often necessary to add a buffer such as disodium hydrogen phosphate.[4] Despite its powerful reactivity and usefulness, 85% or higher hydrogen peroxide, of which the grade is now not widely available, is employed in most TFPAA oxidations. Few alternatives, including the use of urea-hydrogen peroxide complex, have been studied to overcome this problem.[5]

Table 1. Oxidation of ketones to esters with sodium percarbonate and TFAA

Entry	Substrate	Product	Time (hr)	%Yield[a]
1			2	84(94)[b]
2			2	96
3			1.5	96
4			0.67	72(82)[b]
5			2.5	87
6			5	67(99)[b]
7			20	56(98)[b]

[a] all yields are isolated ones. [b] Yields in the parentheses are based upon recovered starting materials.

Here, we report an alternative way of generating TFPAA, which uses sodium percarbonate and trifluoroacetic anhydride (TFAA). Sodium percarbonate is a safe and versatile oxidizing agent, which is commercially available and cheap.[6] In fact, Sodium percarbonate in acidic media showed that the Baeyer-Villiger oxidation was effective for cyclic ketones. But simple alicyclic ketones were not suitable substrates under this condition and deactivated ketones required long reaction times.[7] In our condition, TFAA is added to sodium percarbonate in dichloromethane at room temperature to generate TFPAA *in situ* and an extra buffering agent is not necessary due to the sodium carbonate contained in the reagent.[8]

Table 1 is given above to show our results, which were obtained from the reaction with various ketones. 6-Phenyl-2-hexanone (run 1), which is not an easy substrate for the Baeyer-Villiger oxidation, was converted to the desired acetate within 2 hrs in a high yield. The reaction of other acyclic ketones (runs 2 and 3) also provided desired products in excellent yields. Deactivated ketones such as 4-methoxyacetophenone and benzophenone are similarly oxidized to give desired esters in good yields in relatively short reaction times. In several examples (runs 1, 4, 6 and 7), conversion was not complete in reaction times indicated. But the oxidation was quite clean and yields were high based upon recovered starting materials.

Typical procedure is as follows. To a stirred solution of adamantyl methyl ketone (100 mg, 0.56 mmol) and sodium percarbonate (1.2 g, 9.0 mmol) in 8 ml of dichloromethane was added trifluoroacetic anhydride (320 μL, 2.2 mmol) dropwise at room temperature. The resulting mixture was stirred for 1.5 hrs and quenched with sat. $NaHCO_3$ solution. The aqueous phase was extracted with dichloromethane and the combined organic layers were washed with H_2O and dried over $MgSO_4$. Concentration followed by purification on silica gel (elution with 5% EtOAc in hexane) yielded desired adamantyl acetate (104 mg, 96%).

In conclusion, the present procedure provides a useful and effective alternative to concentrated hydrogen peroxide for the *in situ* generation of trifluoroperoxyacetic acid. Its application to the synthesis of natural product is currently under way.

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References

1. For reviews see: (a) Hassall, C. H. *Org. React.* **1957**, *9*, 73. (b) Plesnicar, B. In *Oxidation in Organic Chemistry*; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; part C, p 254. (c) Hudlicky, L. *Oxidations in Organic Chemistry*; American Chemical Society: Washington, DC, 1990, p 186; Krow, G. R. In *Comprehensive Organic Chemistry*. (d) Trost, B. M.; Fleming, I., Ed.; Pergamon Press: Oxford, 1991; Vol 7, p 671.
2. Emmons, W. O.; Lucas, G. B. *J. Am. Chem. Soc.* **1955**, *77*, 2287.
3. (a) White, R. W.; Emmons, W. D. *Tetrahedron* **1961**, *17*, 31. (b) McClure, J. D.; Williams, P. H. *J. Org. Chem.* **1962**, *27*, 24. (c) Adam, W.; Rodriguez, A. *J. Org. Chem.* **1979**, *44*, 4969. (d) Suzuki, M.; Takada, H.; Noyori, R. *J. Org. Chem.* **1982**, *47*, 902. (e) Matsubara, S.; Takai, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2029.
4. Whitesell, J. K.; Matthews, R. S.; Helbling, A. M. *J. Org. Chem.* **1978**, *43*, 784.
5. (a) Anastasia, M.; Allevi, P.; Ciuffreda, P.; Fiecchi, A.; Scala, A. *J. Org. Chem.* **1985**, *50*, 321. (b) Cooper, M. S.; Heaney, H.; Newbold, A. J.; Sanderson, W. R. *Synlett* **1990**, 534.
6. Mckillop, A.; Sanderson, W. R. *Tetrahedron* **1995**, *51*, 6145.
7. Olah, G. A.; Wang, Q.; Trivedi, N. J.; Prakash, G. K. S. *Synthesis* **1991**, 739.
8. Sodium percarbonate can be purchased from Aldrich Chem. Co. Ltd. and has a composition of $Na_2CO_3 3/2H_2O_2$. Reaction in the presence of Na_2HPO_4 as an extra buffering agent showed a longer reaction time, compared with a non-buffered reaction.