This study demonstrates singlet oxygen production in the intermolecular reaction of two tertiary alkylperoxy radicals and confirms earlier studies of singlet oxygen production in the reactions of primary and of secondary alkylperoxy radicals. Under the conditions studied, singlet oxygen constitutes only a minor reaction product, being only 1.68–12.4% of the amount predicted by reaction 2 or reaction 4. The data presented are not sufficient to identify a particular reaction mechanism, but a review of the literature does suggest mechanisms which can rationalize the data and thermochemical considerations exclude some mechanisms. Reaction 3 is not sufficiently exothermic to directly form singlet oxygen.[6] Further, it is not clear that the solvent cage effects suggested by Mendenhall and Quinga[16] can overcome this objection. Reaction 4 remains a good explanation for the singlet oxygen production by primary and secondary peroxy radicals. Singlet oxygen may be a direct product of reaction 4 or it may be produced as a consequence of the reaction of ground-state oxygen with an excited triplet ketone produced by reaction 4. For the cumylperoxy radical, two mechanisms likely

$$R_2CO^* + O_2\ (^3\Sigma_g) \rightarrow R_2CO + O_2\ (^1\Delta_g) \qquad (5)$$

account for the singlet oxygen produced. Reaction 2 is the most obvious mechanism. A more complex reaction sequence for the production of singlet oxygen is initiated by the fragmentation of cumylalkoxy radicals produced in reaction 3 to give methyl radicals and acetophenone.[2,3] The methyl radicals rapidly react with oxygen to give methylperoxy radicals which then react via reaction 4 to give singlet oxygen. For *tert*-butyl peroxy radicals the singlet oxygen most likely results from reaction 2, since β-scission of *tert*-butylalkoxy radicals produced in reaction 3 is less favored than is the fragmentation of cumylalkoxy radicals.[3]

Experimental Section

Chemiluminescent Spectrometer. The infrared chemiluminescene spectrometer used and the method of calibration of singlet oxygen yields using the hydrogen peroxide + hypochlorous acid reaction have been described previously.[11,12,15] Spectral analysis was done by using a series of interference filters.[15]

Chemicals and Reagents. Ceric ammonium nitrate, *tert*-butyl hydroperoxide, cumyl hydroperoxide, and deuterium oxide, 99.8%, were obtained from Sigma Chemical Co. Ethyl hydroperoxide, 10% aqueous solution, was obtained from Polysciences, Inc. Hydrogen peroxide, 30% stabilized reagent, was a product of J.T. Baker Chemical Co. Ethyl hydroperoxide and hydrogen peroxide were assayed by using the method of Cotton and Dunford.[17] Cumyl hydroperoxide and *tert*-butyl hydroperoxide were assayed by iodide ion oxidation in acetic acid using hydrogen peroxide as a standard. The excess iodide ion was complexed with cadmium ion prior to the measurement of absorbance at 358 nm.[18] Hydroperoxylinoleic acid was enzymatically synthesized from linoleic acid by using soybean lipoxygenase at 0 °C in the presence of excess oxygen.[19] About 90% of the hydroperoxide produced was the 13-hydroperoxy isomer.[19] The product had no discrete absorption band at 280 nm. The hydroperoxide was assayed by absorbance at 234 nm by using an extinction coefficient of $2.5 \times 10^4\ M^{-1}\ cm^{-1}$.[20] Hypochlorous acid was purified and assayed as previously described.[15] Other inorganic chemicals were reagent grade. Water was glass distilled.

Reaction Conditions. All experiments were done at 25 °C in air-saturated solutions. Many experiments were done in deuterium oxide, which greatly enhanced the singlet oxygen emission. Ceric ammonium nitrate in 1.5 mL of 20 mM hydrochloric acid solution was placed in the spectrometer. The reaction was then initiated by the rapid injection of an additional 1.5 mL of hydrochloric acid solution containing the hydroperoxide to be studied.

Statistical Analysis. Unless otherwise specified, all experiments were done in triplicate and were reported as the mean ± the standard error.

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Registry No. O_2, 7782-44-7; ethyl hydroperoxide, 3031-74-1; 13-hydroperoxylinoleic acid, 23017-93-8; *tert*-butyl hydroperoxide, 75-91-2; cumyl hydroperoxide, 80-15-9; hydrogen peroxide, 7722-84-1; ceric ammonium nitrate, 16774-21-3.

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A Convenient Procedure for the Monosilylation of Symmetric 1,*n*-Diols

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Bifunctional reagents are important synthons for the organic chemist. Many of these reagents (**3**) have as their starting material symmetric 1,*n*-diols (**1**). The crucial step in the production of the bifunctional reagent (**3**) is often the monoprotection of the diol (**1** → **2**). While numerous

$$\underset{\mathbf{1}}{HO(CH_2)_nOH} \rightarrow \underset{\mathbf{2}}{HO(CH_2)_nOR} \rightarrow \underset{\mathbf{3}}{X(CH_2)_nY}$$

methods have been developed for the selective protection of unsymmetric diols, for example, protection of a primary alcohol in the presence of a secondary alcohol, the selective monoprotection of symmetric diols can still present a problem.[1] In general if stoichiometric equivalents of protecting reagent to diol are utilized, a statistical mixture of unprotected, monoprotected, and diprotected products result in which the yield of the desired monoprotected material is only 50%.[2] To date this statistical pitfall has been circumvented most easily by employing a large excess of the starting diol relative to the protecting reagent. This produces an acceptable yield of the monoprotected product based on the protecting reagent as the limiting reagent.[3] The excess diol, if inexpensive, is simply discarded or, if expensive, can be recycled via chromatography. Other more esoteric solutions to the problem of selective protection include the use of polymer supports[1] and the use of continuous solvent extraction to remove the desired monoprotected product.[4] In this paper we wish to report

(1) For a discussion of this problem, see: Leznoff, C. C. *Acc. Chem. Res.* **1978**, *11*, 327 and references therein.
(2) Reaction of symmetrical diols with thallium alkoxide in a Williamson ether synthesis have shown some selectivity toward monoprotected material, see: Kalinowski, H. O.; Crass, G.; Seebach, D. *Chem. Ber.* **1981**, *114*, 477.
(3) For some applications of this methodology, see: (a) Sheehan, M.; Spangler, R. J.; Djerassi, C. *J. Org. Chem.* **1971**, *36*, 3526. (b) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4743. (c) Ikeda, J.; Ikeda, N.; Yamamoto, H. *Tetrahedron Lett.* **1984**, *25*, 5177.

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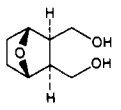
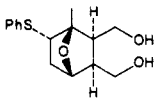
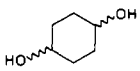
Table I. Monosilylation of Symmetric 1,*n*-Diols

entry	diol	conditions[a]	product (yield, %)[b,c]
	$HO(CH_2)_nOH$		$HO(CH_2)_nOSiMe_2$-*t*-Bu/t-$BuMe_2SiO(CH_2)_nOSiMe_2$-*t*-Bu
1	**4a** (n = 2)	A	**4b** (82)
2	**5a** (n = 3)	A	**5b** (90)
3	**6a** (n = 4)	A	**6b** (97)
4	**7a** (n = 5)	A	**7b** (87)
5	**7a** (n = 5)	C	**7b** (54)/**7c** (23)
6	**8a** (n = 6)	A	**8b** (90)
7	**9a** (n = 10)	B	**9b** (75)/**9c** (9)
8	**9a** (n = 10)	C	**9b** (46)/**9c** (24)
9	 **10a**	A	**10b** (89)
10	 **11a**	A	**11b** (96)[d]
11	 **12a**[e]	B	**12b** (57)/**12c** (13)

[a] Procedures A and B both utilize diol (1.0 equiv), sodium hydride (1.0 equiv), and *tert*-butyldimethylsilyl chloride (1.0 equiv). Procedure C utilizes diol (1.0 equiv), *tert*-butyldimethylsilyl chloride (1.0 equiv), Et_3N, and DMAP (see Experimental Section for full details). [b] If only one product is listed it represents monosilylated material. If two products are listed the major product is monosilylated and the minor product is bissilylated. [c] All yields are for purified material. [d] This compound was isolated as a 60:40 mixture of two monosilylated isomers (see ref 15). [e] The commercial mixture of cis/trans isomers was used.

on a simple modification of the silylation reaction which produces high yields of monosilylated material even when stoichiometric equivalents of diol and silylating agent are utilized. This procedure allows for the efficient use of the diol moiety without resorting to costly and time-consuming recycling procedures.

Faced with the task of monoprotecting the bicyclic diols **10a** and **11a** (see Table I) we found that many of the standard protecting methods produced unacceptable ratios of monoprotected material relative to starting diol and diprotected material.[5] In due course, however, we attempted to silylate the monosodium alkoxide salt (NaH, 1.0 equiv) with 1 equiv of *tert*-butyldimethylsilyl chloride (*t*-$BuMe_2SiCl$) and were rewarded with excellent yields of monosilylated material (Table I, entries 9 and 10). In an effort to explore the generality of this reaction we silylated the commercially available 1,*n*-primary diols (n = 2–6, 10). As seen in Table I these examples yielded equally rewarding results. Even when the alcohol centers were separated by 10 carbons (entry 7) our method out-performed the more traditional silylating procedure[6] (entry 8). A direct comparison of silylation conditions is also made in entries 4 and 5 (n = 6), and again the sodium alkoxide methodology is clearly superior. Extension of this methodology to symmetrical secondary diols (entry 11) has proved less successful although some selectivity is still observed.[7] It should be noted that the products arising from diols **5a**,[3b] **6a**,[3c,8] and **7a**[8] have already found use as precursors to bifunctional reagents. In all three cases the previous preparations used an excess of diol to assure good yields of monosilylated products.

The source of this selectivity may reside in the properties of the monosodium salt **13** of the diol. Treatment of the diols (generalized in structure **1**) with 1 equiv of NaH causes the formation of a voluminous precipitate. Based

$$\underset{\mathbf{1}}{HO(CH_2)_nOH} \rightarrow \underset{\mathbf{13}}{HO(CH_2)_nONa} \rightarrow \underset{\mathbf{14}}{HO(CH_2)_nOSiMe_2\text{-}t\text{-}Bu}$$

on the observation that the potassium t-butoxide/t-butanol complex is considerably less soluble in ethereal solvents than pure potassium *tert*-butoxide,[9] we believe this precipitate is an aggregate of the monosodium salt **13**.[10] This precipitation phenomena effectively removes any basic species from the reaction mixture. Upon the addition of silylating agent the small amount of dissolved alkoxide salt is silylated. As more salt slowly goes into solution, the rate of silylation of alkoxide **13** is faster than the rate of proton transfer between the alkoxide salt **13** and the already formed silyl alcohol **14**.[11] The sluggishness of proton transfer is at least partially due to the low concentration of alkoxide salt. The fact that the monosilyated alcohol is not formed instantaneously upon addition of the silylating agent also bespeaks for a slow dissolution of the precipitated alkoxide complex. Within the context of this scenario the poorer performance of the secondary diol could be blamed on the increased basicity of the secondary alkoxide coupled with the expected slower silylation of the secondary center.

In conclusion a simple method for the selective monosilylation of symmetrical primary diols has been discovered. Importantly this method makes efficient use of both the diol and protecting reagent. Furthermore the concept which underlies the observed selectivity may be useful in designing other types of selective reaction processes.

Experimental Section

General Procedures. The IR spectra were obtained on a Perkin-Elmer Model 299 spectrophotometer. The ^1H NMR spectra were determined with a Varian Model T-60A NMR spectrometer (60 MHz) or with a Bruker Model WM-300 NMR spectrometer (300 MHz). The chemical shift values are expressed in δ values (ppm) with Me_4Si as an internal standard. The mass spectra were obtained with a Varian MAT Model 112S mass

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(5) For diol **11a** typical silylation conditions (procedure C, Table I and esterification conditions (PhC(O)Cl (1.0 equi), pyridine) actually favored diprotected/diol products relative to monoprotected product.

(6) Chaudhary, S. K.; Hernandez, O. *Tetrahedron Lett.* **1979**, 99.

(7) The mild selectivity observed for the secondary diol **12a** may reflect the bias of this diol rather than a selectivity associated with our procedure. More traditional protection methods exhibit a similar selectivity for monoprotected material, see: Prins, D. A. *Helv. Chem. Acta* **1957**, *40*, 1621 and references therein.

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(9) House, H. O.; Roelofs, W. L.; Trost, B. M. *J. Org. Chem.* **1966**, *31*, 646 (footnote 5). We wish to thank Prof. House for bringing this to our attention.

(10) The exact nature of this aggregate (dimer, tetramer, higher oligomers) is not known and could vary depending on the diol structure. For diols **9a** and **12a** we suspect some diol may be occluded in the precipitated aggregate as higher temperatures and longer reaction times (conditions B, Table I) are necessary to get complete deprotonation.

(11) If fast proton transfer were to occur the normal statistical mixture of products would result.

(12) The known diol **10a** was prepared from the commercially available adduct of furan and maleic anhydride as previously described (ref 13). Diol **11a** was prepared in an analogous sequence starting from the Diels–Alder adduct of 2-methyl-3-thiophenoxyfuran (ref 14).

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(15) Although not important in the context of this note, we have assigned the major isomer as the product with the silyl group on the oxygen farthest away from the bridgehead methyl group.

spectrometer. All reactions were run under a nitrogen atmosphere. All ethereal solvents were freshly distilled from sodium benzophenone ketyl. Flash chromatography was performed with silica gel from E. Merck (Kieselgel 60, 200–400 mesh). Diols **4a**, **5a**, **6a**, **7a**, **8a**, **9a**, and **12a** were all purchased from Aldrich Chemical Co. and used without further purification. Diols **10a** and **11a** were prepared according to the literature precedent.[12]

General Procedures Used for the Preparation of Siloxy Alcohols. Procedure A. Sodium hydride (0.27 g, 5.6 mmol) was suspended in THF (11 mL) after being washed with hexane. The diol (5.6 mmol) was added to this mixture at room temperature and stirred for 45 min at which time a large amount of an opaque white precipitate had formed. The *tert*-butyldimethylsilyl chloride was then added, and vigorous stirring was continued for 45 min. The mixture was poured into ether (100 mL), washed with 10% aqueous K_2CO_3 (30 mL) and brine (30 mL), dried (Na_2SO_4), and concentrated in vacuo. The resulting oil was purified by flash chromatography using ethyl acetate/hexane mixtures as eluent (see spectroscopic data for the exact ratio used in each case).

Procedure B. The same general experimental is followed as in procedure A except that the diol and NaH were heated together at 55 °C for 18 h prior to the addition of *tert*-butyldimethylsilyl chloride at room temperature. The silylation of diol **9a** was carried out for 2 h at room temperature, while diol **12a** was silylated for 19 h at room temperature. Workup and purification was performed as outlined in procedure A.

Procedure C. To the diol (4.81 mmol) in methylene chloride (10 mL) were added sequentially triethylamine (0.7 g, 6.9 mmol), 4-(dimethylamino)pyridine (DMAP, 100 mg), and *tert*-butyldimethylsilyl chloride (4.81 mmol) at room temperature. The mixture was allowed to stir for 4 h and then poured into ether (100 mL), washed with 10% aqueous $NaHSO_4$ (2 × 30 mL) and 10% aqueous K_2CO_3 (30 mL), dried (Na_2SO_4), and concentrated in vacuo. Purification was performed as outlined in procedure A.

Data for the Monosilylated Diols 4b–12b. 4b (30% ethyl acetate/hexane): IR (CCl_4) 3610 (sh), 1390, 1360 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.62 (4 H, m), 2.2 (1 H, br s), 0.82 (9 H, s), 0.06 (6 H, s); MS, *m/e* (relative intensity) 119 (10), 75 (100); calcd for $C_4H_{11}O_2Si$ (M – *tert*-butyl) 119.0528, found 119.0516; CIMS, 177 (M + 1).

5b (30% ethyl acetate/hexane): IR (CCl_4) 3615 (sh), 3550 (br), 1392, 1370 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.80 (2 H, t, J = 6.0 Hz), 3.70 (2 H, br t, J = 6.0 Hz), 2.71 (1 H, br s), 1.78 (2 H, pentet, J = 6.0 Hz), 0.84 (9 H, s), 0.06 (6 H, s); MS, *m/e* (relative intensity) 133 (20), 105 (45), 75 (100); calcd for $C_5H_{13}O_2Si$ (M – *tert*-butyl) 133.0685, found 133.0676; CIMS, 191 (M + 1).

6b (40% ethyl acetate/hexane): IR (CCl_4) 3620 (sh), 3500 (br), 1392, 1365 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.80–3.60 (4 H, br m), 2.50 (1 H, br s), 1.78–1.52 (4 H, br m), 0.81 (9 H, s), 0.04 (6 H, s); MS, *m/e* (relative intensity) 147 (8), 105 (47), 75 (100); calcd for $C_6H_{15}O_2Si$ (M – *tert*-butyl) 147.0841, found 147.0835; CIMS, 205 (M + 1).

7b (30% ethyl acetate/hexane): IR (CCl_4) 3640 (sh), 3480 (br), 1390, 1360 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.70–3.52 (4 H, m), 2.61 (1 H, br s), 1.75–1.39 (6 H, m) 0.90 (9 H, s), 0.05 (6 H, s); MS, *m/e* (relative intensity) 161 (7), 105 (50), 75 (100), 69 (77); calcd for $C_7H_{17}O_2Si$ (M – *tert*-butyl) 161.0997, found 161.0952; CIMS, 219 (M + 1).

8b (30% ethyl acetate/hexane): IR (CCl_4) 3615 (sh), 1390, 1360 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.75–3.42 (4 H, br m), 2.25 (1 H, br s), 1.62–1.41 (8 H, br s), 0.80 (9 H, s), 0.04 (6 H, s); MS, *m/e* (relative intensity) 175 (5), 105 (25), 83 (50), 75 (100); calcd for $C_8H_{19}O_2Si$ (M – *tert*-butyl) 175.1154, found 175.1161; CIMS, 233 (M + 1).

9b (25% ethyl acetate/hexane): IR (CCl_4) 3640 (sh), 1390, 1360 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 3.75–3.55 (4 H, m), 2.10 (1 H, s), 1.60–1.45 (16 H, br s), 0.95 (9 H, s), 0.06 (6 H, s); MS, *m/e* (relative intensity) 231 (8), 105 (35), 75 (100); calcd for $C_{12}H_{27}O_2Si$ (M – *tert*-butyl) 231.1780, found 231.1774; CIMS, 289 (M + 1).

10b (30% ethyl acetate/hexane): IR (CCl_4) 3640 (sh) 3480 (br), 1390, 1360 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.21 (1 H, br d, J = 2.6 Hz), 4.17 (1 H, br d, J = 3.0 Hz), 3.68 (1 H, A of an ABX, dd, J = 10.4, 9.0 Hz), 3.66 (1 H, m), 3.58 (1 H, B of an ABX, dd, J = 10.4, 5.6 Hz), 3.49 (2 H, m, includes OH), 2.07 (2 H, m), 1.63 (2 H, m), 1.42 (2 H, m), 0.81 (9 H, s), 0.02 (6 H, s); MS, *m/e* (relative intensity) 215 (4), 105 (40), 75 (100); calcd for $C_{10}H_{19}O_3Si$ (M – *tert*-butyl) 215.1103, found 215.1093; CIMS, 273 (M + 1).

11b (25% ethyl acetate/hexane), major isomer[15] (elutes first): IR (CCl_4) 3640, 3480, 1390, 1382, 1361 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (2 H, dd, J = 7.2, 1.5 Hz), 7.19–7.07 (3 H, m), 4.05 (1 H, d, J = 5.6 Hz), 3.77 (1 H, t, J = 10.0 Hz), 3.66–3.49 (4 H, m), 3.12 (1 H, dd, J = 11.1, 5.3 Hz), 2.82 (1 H, td, J = 9.0, 4.2 Hz), 2.41 (1 H, td, J = 11.1, 5.6 Hz), 2.23 (1 H, td, J = 9.0, 5.5 Hz), 1.39 (1 H, dd, J = 11.9, 5.3 Hz), 1.12 (3 H, s), 0.80 (9 H, s) 0.01 (6 H, s); MS, *m/e* (relative intensity) 337 (7), 262 (44), 231 (92), 139 (100), 105 (49), 75 (70); calcd for $C_7H_{25}O_3SiS$ (M – *tert*-butyl) 336.9952, found 336.9941.

11b, minor isomer[15] (elutes second): IR (CCl_4) 3640 (sh), 3475 (br), 1390, 1382, 1361 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (2 H, dd, J = 7.1, 1.5 Hz), 7.30–7.21 (3 H, m), 4.21 (1 H, d, J = 5.5 Hz), 3.87–3.57 (5 H, m), 3.22 (1 H, dd, J = 11.1, 5.2 Hz), 2.88 (1 H, td, J = 9.1, 5.2 Hz), 2.50 (1 H, td, J = 11.8, 5.5 Hz), 2.33 (1 H, td, J = 8.7, 4.6 Hz), 1.50 (1 H, dd, J = 12.5, 5.2 Hz), 1.18 (3 H, s), 0.92 (9 H, s), 0.13 (3 H, s), 0.11 (3 H, s); MS, *m/e* (relative intensity) 376 (12), 337 (4), 253 (61), 231 (66), 75 (100); calcd for $C_{17}H_{25}O_3SiS$ (M – *tert*-butyl) 336.9952, found 336.9939.

12b (cis/trans isomers) (25% ethyl acetate/hexane): 3695 (sh), 3620 (sh), 1380, 1368, 1355 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 3.9–3.4 (2 H, br m), 2.76 (1 H, br s), 1.9–1.4 (8 H, m), 0.90 (9 H, s), 0.02 (6 H, s); MS, *m/e* (relative intensity) 173 (4), 81 (100), 75 (58); calcd for 173.1001, found 173.1021; CIMS, 231 (M + 1).

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Registry No. **4a**, 107-21-1; **4b**, 102229-10-7; **5a**, 504-63-2; **5b**, 73842-99-6; **6a**, 110-63-4; **6b**, 87184-99-4; **7a**, 111-29-5; **7b**, 83067-20-3; **7c**, 77572-86-2; **8a**, 629-11-8; **8b**, 103202-59-1; **9a**, 112-47-0; **9b**, 90934-00-2; **9c**, 103202-64-8; **10a**, 55423-53-5; **10b**, 103202-60-4; **11a**, 103202-58-0; **11b** (major isomer), 103202-61-5; **11b** (minor isomer), 103202-65-9; *cis*-**12a**, 931-71-5; *trans*-**12a**, 6995-79-5; *cis*-**12b**, 103202-62-6; *trans*-**12b**, 103202-63-7; *cis*-**12c**, 103202-66-0; *trans*-**12c**, 103202-67-1; *tert*-butyldimethylsilyl chloride, 18162-48-6.

Facile Anhydride Synthesis Using Trichlorotrifluoroacetone Hydrate

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Several successful methods are available for synthesizing carboxylic acid anhydrides,[1-5] but each of these methods has one or more of the following shortcomings: unstable or special reagents need to be prepared, extra steps are needed to remove side products, or yields are low for some anhydrides.

Here a simple reaction at room temperature forming volatile side products is presented for synthesizing carboxylic acid anhydrides. The key reagent, 1,1,1-trichloro-3,3,3-trifluoroacetone,[6] is commercially available,

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