Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 1655–1657

TETRAHEDRON LETTERS

Direct formation of cyclic sulfates utilising hypervalent iodine species and sulfur trioxide adducts

Richard I. Robinson and Simon Woodward*

School of Chemistry, The University of Nottingham, Nottingham NG7 2RD, UK

Received 6 November 2002; revised 9 December 2002; accepted 20 December 2002

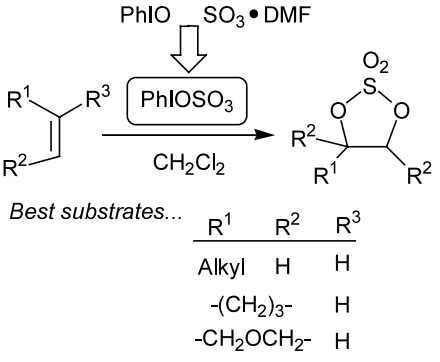
Abstract—PhIO reacts with SO_3·DMF at 0°C to form an active sulfating reagent; subsequent addition of alkenes results in the direct formation of cyclic sulfates in moderate to good yield (35–75%). Terminal, 1,1-disubstituted and cyclopentenes participate in the reaction which is technically very straightforward to carry out.

Cyclic sulfates are an important class of vicinally substituted electrophile with a comparable role to epoxides in modern organic synthesis.[1] Unfortunately, the direct and simple preparation of cyclic sulfates from alkenes is limited to a handful of papers. Copper-promoted $K_2S_2O_8$ oxidations[2] and iodine(III)/SO_3 gas reagents[3] have both been shown to be of use in these transformations. The former reaction gives the sulfates in low yield, generally as part of a product mixture. The latter use of iodosylbenzene with sulfur trioxide gas was first reported by Zefirov and co-workers[4] but the difficulty of handling and drying of sulfur trioxide gas means this reaction has not been fully exploited. More recently the use of trimethylsilyl chlorosulfonate as an alternative source of sulfur trioxide has been shown to be successful.[5] This procedure gave improved yields over the sulfur trioxide gas method, however, it still involved the use of low temperatures and the removal of trimethylsilyl chloride and solvent to form the phenyliodosulfate reagent. The electrophilic character of iodine in iodosylbenzene is greatly increased by the addition of Lewis acids such as boron trifluoride and sulfur trioxide. Cycloalkenes have been demonstrated to undergo ring contraction, to give formylated products under such conditions.[6]

We were interested in developing a new, simple, one-pot procedure using commercially available sulfur trioxide adducts, applicable for a range of alkenes, that afforded reaction mixtures amenable to further immediate synthesis (Scheme 1). We found that the reaction of iodosylbenzene with the dimethylformamide·sulfur trioxide adduct in dichloromethane at room temperature produces phenyliodosulfate (as an insoluble polymer) in quantitative yield. The gum like residue disappears completely upon addition of the alkene substrate in 10–30 min at room temperature, depending on the substrate reactivity, and provides useful yields of cyclic sulfates (Table 1).

The reactions are all extremely clean, with complete conversion of the alkene substrate by ^{1}H NMR and GC analysis, the only by-products being dimethylformamide and iodobenzene. The isolated yields often reflect the stability of the cyclic sulfate under the filtration chromatography required to remove iodobenzene, rather than the intrinsic reaction success. The sulfates can be reacted on as crude reaction mixtures in many cases without the need for isolation.

The alkene substrates in Table 1 can be run at either room temperature or 0°C. While most of our reactions



Scheme 1. Direct formation of cyclic sulfates in this report.

* Corresponding author. Tel.: +44-115-9513541; fax: +44-115-9513564; e-mail: simon.woodward@nottingham.ac.uk

0040-4039/03/$ - see front matter
PII: S0040-4039(03)00039-X

Table 1. Isolated yields of cyclic sulfates from Scheme 1

R^1	R^2	R^3	Yield (%)[a]
Bu^n	H	H	70
$C_6H_{13}^n$	H	H	75
Et	H	Et	65
$-CH_2OCH_2-$		H	66
$-(CH_2)_3-$		H	43
$Br(CH_2)_2$	H	H	42
$Ph(CH_2)_4$	H	Me	35

[a] Isolated yield. Experimental procedure: Under an argon atmosphere iodosobenzene (220 mg, 1.0 mmol), was stirred in *dry* DCM (2 ml) until a free-flowing yellow suspension resulted. Sulfur trioxide·DMF complex (~153 mg, 1.0 mmol) was then added promptly. After approximately 10 min a viscous yellow gum separates. The alkene (0.7 mmol) was added and the reaction mixture stirred at room temperature until the phenyliodosulfate dissolved. The crude sulfate was used directly or isolated by removal of the solvent under reduced pressure and filtration chromatography [eluting with CH_2Cl_2/light petroleum 1:4 to remove iodobenzene, and flushing with DCM to obtain the cyclic sulfate, often as a colourless oil].

were run with a slight excess of phenyliodosulfate this was not a requirement, similar yields were attained using a stoichiometric amount of olefin. Many of the isolated sulfates are unstable at room temperature over a matter of weeks. However, they can be stored under an inert atmosphere in chlorinated solvent at 0°C for at least 3 months. Interestingly it was possible, when using an excess of phenyliodosulfate to carry out a reaction, to syringe out the products and carry out a secondary reaction with a different substrate indicating that product decomposition by excess $PhIOSO_3$ is not an issue.

Attempted sulfation of cyclohexene, cyclooctene, styrene, and *cis*/*trans* stilbene, failed due to decomposition of the sulfate under the standard reaction conditions. Further investigation is currently underway but we note that 1,2-diphenylethene cyclic sulfate has been prepared previously by Sharpless,[7] via oxidation of the cyclic sulfite, and is reported to be unstable above 0°C. In our case lowering the temperature did not yield the desired sulfate, and at temperatures below −30°C no reaction was observed at all. It has been reported that *trans*-stilbene undergoes a rearrangement in the presence of sulfur trioxide and iodosylbenzene to give diphenylacetaldehyde.[8] However, we saw no evidence of this. 1,2-Dihydronapthalene gave a low yield of the cyclic sulfate (15%), but also produced unidentified side products during the reaction.

Only the dimethylformamide·sulfur trioxide adduct was found to be successful in the transformation, whereas the trimethylamine and pyridine SO_3 adducts gave no product and trace amounts, respectively. Cordero and co-workers have also found that SO_3·DMF complex exhibits different reactivity in aminosulfonation of olefins, compared with related amine adducts.[9] Sulfur trioxide has been shown to form β-sultones directly from olefins,[10] however, we found that 1-hexene exhibited no such reactivity towards the dimethylformamide sulfur trioxide complex at room temperature in dichloromethane.

In conclusion we have found a simple version of the Zefirov reaction which should significantly improve the utility of this process.[11] Further improvements are being sort in our laboratory at present.

Acknowledgements

We thank EPSRC for support and a studentship (R.I.R.) through GR/N09824/01 and for access to their Mass Spectrometry Service. We are grateful to the COST-D24 programme for additional EU support.

References

1. Overview: Lohray, B. B.; Bhushan, V. *Adv. Heterocycl. Chem.* **1997**, *68*, 86–180.
2. Perumal, P. T. *Synth. Commun.* **1990**, *20*, 1353–1356.
3. Zefirov, N. S.; Sorokin, V. D.; Zhdankin, V. V.; Kozmin, A. S. *Zh. Org. Khim.* **1986**, *22*, 450–452.
4. Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Yu. V.; Caple, R.; Berglund, B. A. *Tetrahedron Lett.* **1986**, *27*, 3971–3974.
5. Bassingdale, A. R.; Katampe, I.; Taylor, P. G. *Can. J. Chem.* **2000**, *78*, 1479–1483.
6. Varvoglis, A. *Hypervalent Iodine Reagents in Organic Synthesis*; Academic Press: San Diego, 1996, pp. 80 and 216 and references cited within.
7. Oi, R.; Sharpless, B. K. *Tetrahedron Lett.* **1991**, *32*, 999–1002 and references cited within.
8. Zefirov, N. S.; Caple, R.; Palyulin, B.; Berglund, B.; Tykwinski, R.; Zhdankin, V. V.; Kozmin, A. S. *Izv. Akad. Nauk., SSSR* **1988**, 1452–1453.
9. Cordero, F. M.; Cacciarini, M.; Machetti, F.; De Sarlo, F. *Eur. J. Org. Chem.* **2002**, 1407–1411.
10. Roberts, D. W.; Williams, D. L. *Tetrahedron* **1987**, *43*, 1027–1062.
11. Selected NMR data for cyclic sulfate products (all ^1H at 400 MHz and ^{13}C at 100 MHz in $CDCl_3$):
From hex-1-ene: δ_H 5.02–4.95 (m, 1H, CHO); 4.71 (dd, 1H, $J=9.0$, 6.0, $CH_{2\alpha}O$); 4.34 (*apparent* t, 1H, $J=6.0$, 6.0, $CH_{2\beta}O$); 1.96–1.91 (m, 1H; $CHCH_{2\alpha}CH_2$); 1.83–1.75 (m, 1H, $CHCH_{2\beta}CH_2$); 1.53–1.31 (m, 4H, chain-CH_2); 0.94 (t, 3H, $J=6.7$, Me). δ_c 83.0, 72.9, 32.0, 26.7, 22.2, 13.8.
From oct-1-ene: δ_H 5.01–4.94 (m, 1H, CHO); 4.71 (dd, 1H, $J=8.6$, 6.0, $CH_{2\alpha}O$); 4.34 (*apparent* t, 1H, $J=8.6$, $CH_{2\beta}O$); 2.00–1.90 (m, 1H, $CHCH_{2\alpha}CH_2$); 1.81–1.71 (m, 1H, $CHCH_{2\beta}CH_2$); 1.55–1.25 (m, 8H, chain-CH_2); 0.89 (t, 3H, $J=6.8$, Me). δ_c 83.1, 72.9, 32.3, 31.8, 29.3, 29.0, 24.6, 22.7.
From 2-ethylbut-1-ene: δ_H 4.42 (s, 2H); 1.93 (m, 4H); 1.02 (t, 6H, $J=7.5$, Me). δ_c 95.8, 74.6, 28.9, 7.4.
From 2,5-dihydrofuran: δ_H 5.40 (*apparent* dd, 2H, $J=$ 3.0, 1.0); 4.32 (d, 2H, $J=13.0$); 3.72 (*apparent* ddd, 2H, $J=13.0$, 3.0, 1.0). δ_c 83.3, 72.2.
From cyclopentene: δ_H 5.30 (*apparent* dd, 2H, $J=3.0$, 1.0); 2.26–2.20 (m, 2H); 2.08–2.03 (m, 1H); 1.85–1.81 (m, 3H). δ_c 85.8, 32.6, 22.3.

From 4-bromo-but-1-ene: δ_H 5.23 (dddd, 1H; $J=4.7$, 6.2, 7.2, 9.3, CHO); 4.83 (dd, 1H, $J=8.9$, 6.2, $CH_{2\alpha}O$); 4.42 (dd, 1H, $J=8.9$, 7.2, $CH_{2\beta}O$); 3.56–3.50 (m, 2H, CH_2Br); 2.61–2.55 (m, 1H, $CH_{2\alpha}CH_2Br$); 2.27–2.21 (m, 1H, $CH_{2\beta}CH_2Br$). δ_c 80.6, 72.2, 35.3, 26.7.

From 6-phenyl-2-methyl-hex-1-ene: δ_H 7.30 (dd, 2H, $J=$ 8.0, 1.0, Ph_o); 7.20–7.17 (m, 3H, Ph_{m+p}); 4.43 (d, 1H, $J=9.0$, $CH_{2\beta}$); 4.36 (dd, 1H, $J=9.0$, 1.7, $CH_{2\alpha}$); 2.66 (t, 2H, $J=8.0$, $PhCH_2$); 2.01–1.92 (m, 1H, $CHCH_{2\alpha}$-chain); 1.88–1.80 (m, 1H, $CHCH_{2\beta}$-chain); 1.73–1.68 (m, 2H, chain-CH_2); 1.62 (s, 3H, Me); 1.50–1.47 (m, 2H, chain-CH_2). δ_c 141.8, 128.5, 128.4, 126.0, 92.8 (C), 76.7, 38.4, 35.5, 31.2, 23.5, 22.9.