The E/Z ratio was determined to be 2:3 by comparing the peak areas of the characteristic signals in the ^{1}H NMR spectrum [E isomer, δ 3.17 (s, 2 H); Z isomer, δ 3.27 (s, 2 H)].[18]

Reaction of (3,7-Dimethylocta-2,6-dienyl)triphenylphosphonium Bromide with AlH_3. A tetrahydrofuran (THF) solution of AlH_3 was prepared by the method of Brown and Yoon.[19] To a solution of **9** (3 mmol) in THF (20 mL) was added 15 mmol of AlH_3 in THF (20 mL) in one portion, and the reaction was continued with stirring for 1 h. By column chromatography on silica gel, 3,7-dimethylocta-1,6-diene[20] was obtained in 86% yield.

Registry No. **1a**, 26146-77-0; **1b**, 21087-29-6; **1c**, 91861-44-8; **1d**, 91861-45-9; **1e**, 91861-46-0; **1f**, 91861-47-1; **1g**, 52378-69-5; **1h**, 91861-48-2; **1i**, 38633-40-8; **4a**, 91861-49-3; **4b**, 91861-50-6; **4c**, 91861-51-7; **4d**, 91861-52-8; **4e**, 91861-53-9; **5a**, 4801-15-4; **5b**, 24626-27-5; **5c**, 91861-54-0; **5d**, 91861-55-1; **5e**, 91861-56-2; **5f**, 25201-67-6; **6**, 91861-57-3; **7**, 88517-96-8; **8**, 91861-58-4; **9**, 64767-93-7; **10**, 91861-59-5; **11**, 91861-60-8; LAH, 16853-85-3; AlH_3, 7784-21-6; $Ph_2C{=}CHCH(CH_3)PPh_3I$, 91861-61-9; $PhCH{=}C(CH_3)CH(CH_3)PPh_3I$, 91861-62-0.

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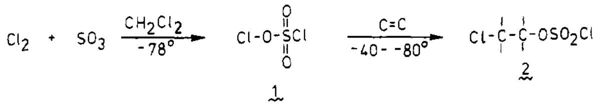
Communications

Chlorine Chlorosulfate: Synthesis and Addition Reactions with Olefins

Summary: Chlorine and sulfur trioxide combine in methylene chloride at −78 °C to form chlorine chlorosulfate (1), a highly electrophilic reagent which adds to olefins to form β-chloroalkyl chlorosulfates 2 (both Markovnikov and anti-Markovnikov adducts).

Sir: In the present communication we describe (i) the novel and readily accessible chlorinating reagent—chlorine chlorosulfate ($ClOSO_2Cl$, **1**)—and (ii) its addition reaction to olefins with formation of 2-chloro-substituted chlorosulfonates **2** in accordance with eq 1. The underlying concept suggests a new approach to the activation of electrophilic reagents.

(1) 

$$Cl_2 + SO_3 \xrightarrow[-78^\circ]{CH_2Cl_2} \underset{\mathbf{1}}{Cl{-}O{-}\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}Cl} \xrightarrow[-40 - -80^\circ]{C=C} \underset{\mathbf{2}}{Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OSO_2Cl}$$

The addition of chlorine-containing electrophiles $Cl^{\delta+}{-}X^{\delta-}$, **3**, to double bonds is a useful way for the functionalization of olefins.[1,2] The most powerful chlorinating reagents are those in which X is a very nucleofugic group, such as $OClO_3$,[3] $OSeF_5$,[4] OSO_2F,[5] and OSO_2CF_3.[6] However, the application of these reagents is restricted due to both (i) the inconvenient methods for their preparation and explosive and/or dangerous properties and (ii) their exceptional reactivity with typical olefins which prevents formation of normal 1,2-adducts.[7] On the other hand, less reactive reagents of type **3**, e.g., those where X = Hal, NR_2, OR, etc., can react with olefins by both homolytic and heterolytic pathways. The use of polar solvents[1,8] or Lewis acids[2,10] enhance the electrophilic character of these addition reactions. With that in mind, we looked for a new, versatile electrophilic reagent of type **3**, which would be able to add to olefins. We now report that chlorine chlorosulfate **1** satisfies these requirements.

We have found that the addition of equimolar quantities of liquified chlorine (30–40-mmol scale) to a stirred solution of sulfur trioxide in CH_2Cl_2 at −70 °C gives a solution of $ClOSO_2Cl$ which was characterized by the structures of its olefin addition products (vide infra) and by its NQR spectrum.[11] This solution solidified in liquid nitrogen and the so-obtained solid sample exhibits two signals in its ^{35}Cl NQR spectrum for different chlorine atoms at 36.17 MHz (typical for alkyl chlorosulfates[12a]) and 54.0 MHz (this frequency is in the range observed for alkyl hypochlorites[12b]). The solution of **1** in CH_2Cl_2 is ready for reactions with organic substrates and is stable in the absence of moisture for several days at 4 °C.

The resulting solution of **1** was used without purification for addition to several olefins. In all cases an exothermic reaction (temperature was maintained at −40 °C to −85 °C) occurred to give the addition products **4**–**11**, which were isolated and purified either by distillation in vacuo or by fast chromatography on a short column with silica gel. A side reaction forming the corresponding dichlorides was found in some cases, but the purification of the adducts **4**–**11** is easily achieved. The yields and ^{1}H NMR spectra are given in Table I.

The reaction of **1** with ethylene gives 2-chloroethyl chlorosulfate **4**[13] in a high yield. The addition to unsymmetrical olefins such as 1-hexene, methyl methacrylate, or trichloroethylene proceeds to give in each case mixtures of Markovnikov and anti-Markovnikov adducts. Addition

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[7] In fact these reagents were used for the addition to polyfluorinated olefins which do not react with less powerful electrophiles.[3,5,6]

[8] For instance, the application of HCOOH as the solvent for RSCl addition to olefins leads to a miscellanea of new pathways.[9]

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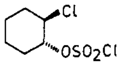
Table I. Addition Products of Chlorine Chlorosulfate 1 to Olefins

olefin	addition product (no.)	% yield	bp (mm), °C	^{1}H NMR, δ
ethylene	$ClCH_2CH_2OSO_2Cl$ (4)	85	58–59 (1)[a]	3.80 t (2 H, J = 5.8 Hz, CH_2Cl), 4.67 t (2 H, CH_2O)
trichloroethylene	$Cl_3CCH(Cl)OSO_2Cl$ (5) $Cl_2CHCCl_2OSO_2Cl$ (6)	56 (5:6 = 1:1)[b]	71–72 (2)	6.10 s
1-hexene	$C_4H_9CH(Cl)CH_2OSO_2Cl$ (7) $C_4H_9CH(OSO_2Cl)CH_2Cl$ (8)	24 (7:8 = 4:1)	62–63 (0.5)[c]	0.90–2.10 m (C_4H_9), 3.85 d (CH_2Cl of 8), 4.15 m (CHCl of 7), 4.55 d (CH_2O of 7), 5.25 m (CHO of 8)
methyl methacrylate	$CH_2(OSO_2Cl)C(Cl)(CH_3)COOCH_3$ (9) $CH_2(Cl)C(OSO_2Cl)(CH_3)COOCH_3$ (10)	88 (9:10 = 3:1)[b]	80–82 (1)	9: 1.84 s (CH_3), 3.84 s (OCH), 4.50 and 4.80 (AB system, J = 10.0 Hz, CH_2O) 10: 1.91 s (CH_3), 3.84 s (OCH_3) and 3.91 m (CH_2Cl)
cyclohexene	 11	35	65–67 (0.5)[c]	1.30–2.50 m (8 H, CH_2), 4.05 m (1 H, W = 26 Hz, CHCl), 4.80 m (1 H, CHO)

[a] See ref 13. [b] Satisfactory elemental analyses were obtained. [c] Partially decomposed upon distillation in vacuo.

to cyclohexene proceeds stereospecifically to give the trans adduct 11. The data of Table I show that 1 can react with olefins which are different in character. While such reagents as $ClOSO_2F$[5] and $ClOSO_2CF_3$[6] give only unidentified tars with typical olefins,[7] the chlorine chlorosulfate 1 gives the corresponding adducts in these cases. On the other hand, it is sufficiently reactive to give the adducts 5 and 6 with less reactive electron-deficient olefins, such as trichloroethylene even at room temperature. Chlorine chlorosulfate 1 is a versatile and inexpensive reagent,[14] and its addition to olefins is a novel reaction of general character and of potential synthetic utility, especially taking into account that the $ClSO_3$ group is highly nucleofugic.[17,18]

In conclusion we should like to point to the generalization and ramificiation of the studied processes. The ability of sulfur trioxide to insert itself into some particular bonds, e.g., Si-Hal,[20] Cl-F,[21] Ac-F,[22] R_2N-Cl,[23] RS-Cl,[24] etc., is known. This communication demonstrates that the "insertion" product 1 can be used as a reactive electrophile. We hope to exploit this approach for the SO_3-mediated additions of weak electrophiles to olefins[25] as well as for other electrophilic processes.

Registry No. 1, 91948-94-6; 4, 13891-58-2; 5, 91948-95-7; 6, 91948-96-8; 7, 91948-97-9; 8, 91948-98-0; 9, 91948-99-1; 10, 91949-00-7; 11, 91949-01-8; ethylene, 74-85-1; trichloroethylene, 79-01-6; 1-hexene, 592-41-6; methyl methacrylate, 80-62-6; cyclohexene, 110-83-8.

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[18] We have found that the adduct 11 reacts with diethylamine with elimination of the chlorosulfate group as a whole. It is worthy to emphasize also that participation of nucleofugic anions in the final step of electrophilic additions is well documented.[19]

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[25] We have successfully used this strategy for SO_3-mediated addition reactions in the case of R_2NCl[23] (formation of 2-chloroethyl sulfamates), of RSCl–CH_3CN and RSSR–CH_3CN[24] (formation of compounds with the 1-RS-2-acetylaminoethane framework, cf. ref 26), of EtONO[27] (formation of chlorosulfates of 2-hydroxy ketones), and of acyl fluorides (cf. ref 22) (formation of β-substituted ketones).

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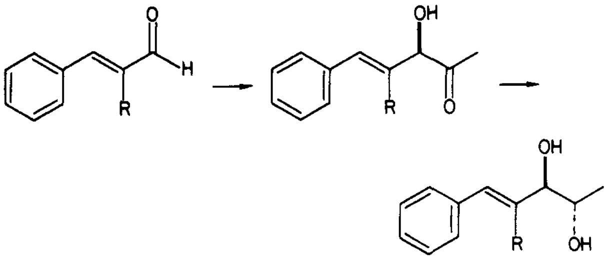
On the Steric Course of Baker's Yeast Reduction of α-Hydroxy Ketones

Summary: The baker's yeast mediated conversion of the α-hydroxy ketones 1–6 into the diols 8–14 is reported.

Sir: The baker's yeast mediated conversion of aromatic α,β-unsaturated aldehydes into the 2*S*,3*R* diols of eq 1 can be viewed as the overall consequence of two distinct chemical operations.[1] (i) Addition of a C_2 unit equivalent of acetaldehyde onto the *si* face of the carbonyl carbon of the α-position unsaturated aldehydes forms (*R*)-α-hydroxy ketones, in an acyloin-type condensation, and (ii) reduction of the latter intermediates on the *re* face of the carbonyl gives rise to the diols actually isolated. Under suitable experimental conditions[2] (*R*)-hydroxy ketones can be ob-



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