added to the structure factor calculations but were not refined. The structure refined to a value of $R = 0.043$. A final difference Fourier plot revealed no missing or extra electron density.

Registry No. 2b, 92056-07-0; **2c**, 92056-08-1; **3**, 92056-09-2; **4**, 92056-10-5; $Cr(CO)_6$, 13007-92-6; (+)-dimethyl L-tartarate, 608-68-4; *o*-nitrobenzaldehyde, 552-89-6.

Supplementary Material Available: Tables of (a) atomic position parameters, (b) atomic thermal parameters, and (c) bond distances and angles of 4 (5 pages). Ordering information is given on any current masthead page.

Lithium Aluminum Hydride Reduction of Allylic Substrates. Notable Leaving Group Effects on the Product Regiochemistry

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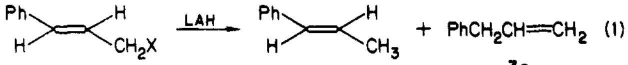
Lithium aluminum hydride (LAH) reduction of allylic halides and their homologues generally proceeds readily to give the S_N2 and/or S_N2' products, the composition being influenced by variable factors.[1] We considered that leaving group effects would be a large, single factor in determining the product regiochemistry[2,3] and, therefore, performed LAH reduction of allylic substrates having a variety of leaving groups.

Treatment of 3-substituted 1-phenyl-1-propenes **1a–c**, having *E* configurations, with LAH gave (*E*)-1-phenyl-1-propene (**2a**; attack by hydride ion at the α-position), while the substrates having poor leaving groups **1d–h** led to the formation of 1-phenyl-2-propene (**3a**; attack at γ-position) together with **2a** (eq 1 and Table I). Triphenylphosphonium salt **1i** afforded exclusively the S_N2' product **3a**. As might be expected, treatment of **1i** with lithium aluminum deuteride yielded 1-phenyl-2-propene-1-*d*. It was also noted that two salts **1f** and **1h** seem to have a similar steric hindrance for hydride-ion attack at the α-position and, nevertheless, these two salts show a significant difference in the reactivity and the regiochemistry; i.e., the reduction of ammonium salt **1f** was considerably slower than that of phosphonium salt **1h**,[4,5] and, moreover, **2a** was predominantly obtained from **1f** and in direct contrast, **3a** was the major product in the case of **1h**.



1 **2a** **3a**

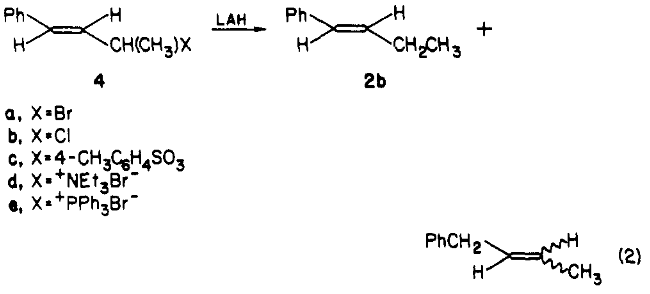
a, $X = Br$
b, $X = Cl$
c, $X = 4\text{-}CH_3C_6H_4SO_3$
d, $X = {}^+SMe_2Br^-$
e, $X = {}^+NEt_3Br^-$
f, $X = {}^+NBu_3Br^-$
g, $X = P(O)(OEt)_2$
h, $X = {}^+PBu_3Br^-$
i, $X = {}^+PPh_3Br^-$

Table I. LAH Reduction of Allylic Substrates[a]

substrate	reaction time, h	products[b] % yield	2/3 ratio	E/Z ratio in 3b
1a	0.5	100	100:0	
1b	0.5	78	100:0	
1c	1	50	100:0	
1d	0.5	90	90:10	
1e	0.5	62	76:24	
1f	6	2[c]	76:24	
1g	0.5	46	2:98	
1h	0.5	90	7:93	
1i	0.5	95	0:100	
4a	1	100	96:4	9:1
4b	1	68	67:38	9:1
4c	1	13[d]	69:31	9:1
4d	5	0[c]		
4e	5	74	0:100	2:3
5a	1	66	100:0	
5b	1	59	100:0	
5c	1	10[d]	74:26	
5d	1	10[c]	39:61	
5e	1	87	74:26	
5f	1	89	0:100	

[a] Reaction with 5 molar equiv of LAH in ether at 20 °C. [b] The isolated yield. Product composition was determined by GLC. [c] The starting material was recovered in a considerable amount. The formation of byproducts was not detected. [d] The corresponding alcohol was isolated in around 70%.

For LAH reduction of 3-substituted 1-phenyl-1-butenes **4a–e** (eq 2) and 3-substituted 1,1-diphenyl-1-propenes **5a–f** (eq 3), similar leaving group effects on the product composition were observed (Table I). Of particular interest is the fact that the triphenylphosphonium salt **5f**, the γ-position of which is extremely crowded, gave exclusively the γ-hydrogenolysis product **3c**. To know the scope of



4 **2b** **3b**

a, $X = Br$
b, $X = Cl$
c, $X = 4\text{-}CH_3C_6H_4SO_3$
d, $X = {}^+NEt_3Br^-$
e, $X = {}^+PPh_3Br^-$

$$\underset{\mathbf{5}}{Ph_2C{=}CHCH_2X} \xrightarrow{LAH} \underset{\mathbf{2c}}{Ph_2C{=}CHCH_3} + \underset{\mathbf{3c}}{Ph_2CHCH{=}CH_2} \quad (3)$$

a, $X = Br$
b, $X = Cl$
c, $X = 4\text{-}CH_3C_6H_4SO_3$
d, $X = {}^+NEt_3Br^-$
e, $X = P(O)(OEt)_2$
f, $X = {}^+PPh_3Br^-$

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(1) (a) Pizey, S. S. "Synthetic Reagents"; Wiley: New York, Vol. 1, 1974. (b) Magid, R. M. *Tetrahedron* **1980**, *36*, 1907.

(2) (a) Treatment of (9-anthrylmethyl)trimethylammonium chloride with LAH gave predominantly 9-methylene-9,10-dihydroanthracene, whereas 9-methylanthracene was the sole product from 9-chloromethylanthracene.[3a] (b) α,γ,γ-Trisubstituted and α,γ-disubstituted allylphosphonates gave exclusively the S_N2' products, the configurations of the alkenes being *E*.[3b] (c) One example has been reported for LAH reduction of α,γ,γ-trisubstituted allyltriphenylphosphonium bromide, in which attack by hydride ion occurs exclusively at the γ-position.[3c] (d) LAH reduction of octyl halides and tosylates in ether revealed that the order of reactivity follows the sequence OTs > I > Br > Cl.[3d] In the case of allylic substrates **1a–c**, however, our preliminary work suggests that the order follows the sequence Br > Cl ≃ OTs.

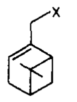
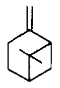
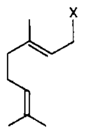
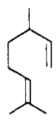
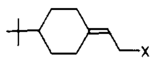
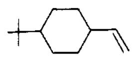
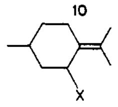
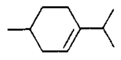
(3) (a) Takagi, M.; Hirabe, T.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1311. (b) Kondo, K.; Negishi, A.; Tsunemoto, O. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 407. (c) Axelrod, E. H.; Milne, G. M.; van Tamelen, E. E. *J. Am. Chem. Soc.* **1970**, *92*, 2139. (d) Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 2550.

(4) Leaving group ability in 1,2-eliminations has been, however, found to follow the sequences $S^+MePh > N^+Me_2Ph > P^+Ph_3$.[5]

(5) Marshall, D. R.; Thomas, P. J.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1975**, 940.

0022-3263/84/1949-4084$01.50/0

Table II. Reaction of Triphenylphosphonium Halides with LAH[a] or AlH_3[b]

substrate	reductant	product	% yield[c]
1i	AlH_3	**3a**	90
4e	AlH_3	**3b**	51[e]
5f	AlH_3	**3c**	98
(*E*)-$PhCH{=}C(CH_3)CH_2X$ (**6**)	LAH	$PhCH_2C(CH_3){=}CH_2$	89
6	AlH_3	$PhCH_2C(CH_3){=}CH_2$	88
(*E*)-$CH_3(CH_2)_7CH{=}CHCH_2X$ (**7**)	LAH	$CH_3(CH_2)_8CH{=}CH_2$	95
7	AlH_3	$CH_3(CH_2)_8CH{=}CH_2$	84
 8	LAH		90
	AlH_3		77
 9	LAH		95
	AlH_3		86
 10	LAH		92
 11			90
$Ph_2C{=}CHCH(CH_3)X$[d]	LAH	$Ph_2CHCH{=}CHCH_3$	70[e]
$PhCH{=}C(CH_3)CH(CH_3)X$[d]	LAH	$PhCH_2C(CH_3){=}CHCH_3$	60[e]

[a] The reaction with 5 molar equiv of LAH in ether at 20 °C for 1 h. [b] The reaction with 5 molar equiv of AlH_3 in tetrahydrofuran at 20 °C for 1 h. [c] The isolated yield. [d] The phosphonium salt was generated in situ by the reaction of the corresponding ylide with methyl iodide. [e] The *E*/*Z* ratio determined by ^1H NMR spectroscopy was about 2:3.

this interesting transformation,[3c] we performed the reaction of a series of phosphonium salts with LAH (Table II). The data clearly indicate that LAH reduction of allylic triphenylphosphonium halides would be a general method to obtain products with allylic migration. Aluminum hydride was also effective for this transformation (Table II).

Experimental Section

Materials. The bromides **1a**, **4a**, and **5a**,[6] chlorides **1b**, **4b**, and **5b**,[7] and tosylates **1c** and **5c**[8] were prepared by the reported methods. On the basis of the large coupling constants (around 16 Hz) between two vinyl protons in ^1H NMR spectra, the starting materials **1a–c** and **4a–b** were confirmed to have *E* configurations.[9,10] The sulfonium salt **1d** (mp 142–145 °C) and ammonium salts **1e** (mp 131–135 °C), **1f** (mp 130–135 °C), **4d** (mp 145–147 °C), and **5d** (mp 195–198 °C) were prepared by treating the corresponding bromides with dimethyl sulfide[11] or with the corresponding trialkylamines.[12] The phosphonium salts **1h** (mp 147–150 °C), **1i** (mp 252–255 °C),[13] **4e** (mp 172–174 °C), **5f** (240–243 °C), **6** (mp 216–218 °C), **7** (mp 88–91 °C), **8** (mp 177–182 °C), **9** (mp 188–189 °C),[14] **10** (mp 192–194 °C), and **11** (mp 148–151 °C) were prepared by the reaction of corresponding bromides with triphenylphosphine in refluxing xylene. The phosphonates **1g** (bp 141–142 °C/2 mmHg) and **5e** [an oil; ^1H NMR δ 1.30 (t, 6 H), 2.51 (q, 2 H), 4.00 (m, 4 H), 5.97 (m, 1 H), 7.00–7.80 (m, 10 H)] were prepared by treating the corresponding bromides with triethyl phosphite.[15]

Reaction of (*E*)-1-Phenyl-3-chlorobutene (4b) with LAH. In a 50-mL flask, equipped with a magnetic stirrer and maintained under N_2, was added a solution of **4b** (500 mg, 3 mmol) in ether (15 mL) by a syringe. Then a solution of LAH (15 mmol) in ether (10 mL) was added in one portion at 20 °C, and the mixture was kept with stirring under slow stream of nitrogen. The mixture was poured into ice-cold HCl and extracted with ether. By column chromatography on silica gel (elution with hexane), a mixture of (*E*)-1-phenyl-1-butene (**2b**)[16] and 1-phenyl-2-butene (**3b**; an *E*-*Z* mixture of ratio 95:5)[17] was obtained in 68% yield (249 mg). The product composition was determined by GLC analysis (SE-30; 1 m).

Treatment of **4b** with lithium aluminum deuteride gave a mixture of 1-phenyl-1-butene-3-*d* and 1-phenyl-2-butene-1-*d*, as was confirmed by analysis with GC–MS and ^1H NMR spectroscopy.

LAH Reduction of (1,2-Dimethyl-3-phenyl-2-propenyl)-triphenylphosphonium Iodide. Butyllithium (12 mmol) in pentane was added to a stirred solution of **6** (4.73 g, 10 mmol) in ether (20 mL) at 20 °C under a positive pressure of N_2 and stirred for 1 h. A solution of methyl iodide (1.35 g, 10 mmol) in ether (5 mL) was added dropwise to the solution and the mixture was kept under reflux for 2 h. Then a solution of LAH (1.90 g, 50 mmol) in ether (20 mL) was added in one portion by a syringe at 20 °C, and the reaction was continued at this temperature for a further 1 h. After conventional workup, the products were column chromatographed on silica gel (elution with benzene–hexane, 1:20) to give 1-phenyl-2-methyl-2-butene (876 mg, 60%).

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(9) The ^1H NMR spectra of *Z* isomers were significantly different from those of the *E* isomers. For example, (*E*)-1-phenyl-3-chloropropene (**1b**): δ 4.12 (d, *J* = 6 Hz, 2 H), 6.16 (t × d, *J* = 16 and 6 Hz, 1 H), 6.52 (d, *J* = 16 Hz, 1 H), 7.20 (m, 5 H). The *Z* isomer: δ 4.14 (d, *J* = 6 Hz, 2 H), 5.80 (t × d, *J* = 10 and 6 Hz, 1 H), 6.56 (d, *J* = 10 Hz, 1 H), 7.20 (m, 5 H).[10a] Similar trends were observed for the isomeric 1-phenyl-1-propenes[10b,c] and 1-phenyl-1-butenes.[16]

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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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[19] Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464.

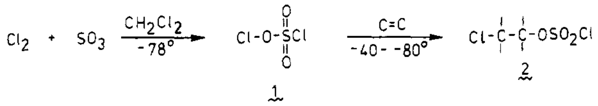
[20] McQuillin, F. J.; Wood, M. *J. Chem. Soc., Perkin Trans. 1*, **1976**, 1762.

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) 

$$Cl_2 + SO_3 \xrightarrow[-78°]{CH_2Cl_2} \underset{1}{Cl{-}O{-}SO_2Cl} \xrightarrow[-40-\,-80°]{C{=}C} \underset{2}{Cl{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OSO_2Cl}$$

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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[11] The NQR spectral data of **1** were obtained in collaboration with Semin, G. K., and his co-workers and will be published separately.

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