Surface-Mediated Reactions. 3. Hydrohalogenation of Alkenes[1]

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Abstract: Appropriately prepared silica gel and alumina have been found to mediate the addition of HCl, HBr, and HI to alkenes. The technique has been rendered even more convenient by the use of various organic and inorganic halides that undergo hydrolysis in the presence of silica gel or alumina to generate hydrogen halides in situ. Under these conditions alkenes such as cycloheptene (**1**), 1-octene (**7**), and 3,3-dimethyl-1-butene (**15**), which react with HCl only very slowly in solution, underwent rapid addition. 1-Octene (**7**) underwent ionic addition of HBr without competing radical addition. 1,2-Dimethylcyclohexane (**24**) afforded the syn addition product **25c**, which underwent equilibration with the thermodynamically more stable isomer **25t**. A mechanism for surface-mediated addition/elimination is proposed involving a stepwise transfer of H^+ and X^- from or to the surface in syn fashion, as shown in Scheme II.

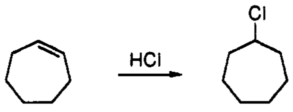
Introduction

Electrophilic addition of hydrogen halides to unsaturated linkages is one of the classical reactions of organic chemistry, having served as the basis for Markovnikoff's well-known rule on the regioselectivity of electrophilic additions,[2] and is of broad synthetic utility. Nonetheless, it is fraught with a number of experimental challenges. Despite numerous implications to the contrary in introductory textbooks,[3,4] HCl does not add to alkenes at preparatively useful rates unless they are strained,[5] highly substituted,[6] or part of a styryl system.[7] HI adds more readily but is difficult to generate and expensive to obtain commercially.[8] HBr also adds readily to most alkenes. However, unless they are highly substituted or part of a styryl system, addition usually involves competing radical-chain addition to give the anti-Markovnikoff product, which predominates unless stringent precautions are taken.[9] Moreover, the generation and transfer of these hygroscopic, gaseous reagents is both inconvenient and difficult to perform stoichiometrically.

We report here that the use of appropriately prepared silica gel or alumina facilitates the hydrochlorination of alkenes, making it possible to readily effect additions that otherwise occur slowly, if at all. Moreover, surface-mediated addition occurs stereoselectively syn and is a simple means of preventing competing radical addition of HBr. Finally, the use of various HX precursors in conjunction with silica gel or alumina is a convenient method for the in situ generation of hydrogen halides.[10]

Results

Hydrochlorination. Treatment of cycloheptene (**1**) with a saturated solution of HCl in CH_2Cl_2 at either 25 or −78 °C afforded no detectable reaction after 1 h (Table I). However, addition of silica gel to the latter reaction mixture resulted in rapid conversion to chloride **2**. More conveniently, simply adding $SOCl_2$, which undergoes hydrolysis to HCl in the presence of silica gel or alumina, to a solution of alkene **1** in CH_2Cl_2 containing a suspension of one of the adsorbents at 25 °C gave chloride **2** rapidly and in high yield.



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To facilitate a systematic study of surface-mediated hydrohalogenations, an optimized small-scale procedure, detailed in the Experimental Section, was developed, involving addition of a specified amount of an HX precursor to a stirred suspension of 2.5 g of Merck grade 40 silica gel or Fisher A540 alumina in 5 mL of CH_2Cl_2 containing 1 mmol of alkene. A procedure was also developed for recycling the silica gel and alumina, which

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[1] Part 2: Breton, G. W.; Daus, K. A.; Kropp, P. J. *J. Org. Chem.* **1992**, *57*, 6646–6649.

[2] Markovnikoff, V. *Compt. Rend.* **1875**, *81*, 668–671.

[3] Commonly used examples include the following: propene, which in the original literature is reported to undergo less than 1% reaction in 4 h;[4a] cyclohexene, for which addition "occurs slowly";[4b] 3-methyl-1-butene, for which addition required 7 weeks for complete conversion[4c] or 1 week for 3–6% conversion and is described as "very slow";[4d] and 3,3-dimethyl-1-butene, which underwent varying degrees of addition over 1 week[4e] and for which addition "proceeds slowly".[4f]

[4] (a) Maass, O.; Sivertz, C. *J. Am. Chem. Soc.* **1925**, *47*, 2883–2891. (b) Fahey, R. C.; Monahan, M. W.; McPherson, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2810–2815. (c) Whitmore, F. C.; Johnston, F. *J. Am. Chem. Soc.* **1933**, *55*, 5020–5022. (d) Pocker, Y.; Stevens, K. D. *J. Am. Chem. Soc.* **1969**, *91*, 4205–4210. (e) Ecke, G. G.; Cook, N. C.; Whitmore, F. C. *J. Am. Chem. Soc.* **1950**, *72*, 1511–1513. (f) Fahey, R. C.; McPherson, C. A. *J. Am. Chem. Soc.* **1969**, *91*, 3865–3869.

[5] (a) Schmerling, L. *J. Am. Chem. Soc.* **1946**, *68*, 195–196. (b) Kwart, H.; Miller, R. K. *J. Am. Chem. Soc.* **1956**, *78*, 5008–5011. (c) Stille, J. K.; Sonnenberg, F. M.; Kinstle, T. H. *J. Am. Chem. Soc.* **1966**, *88*, 4922–4925. (d) Cristol, S. J.; Caple, R. *J. Org. Chem.* **1966**, *31*, 2741–2748. (e) Brown, H. C.; Liu, K.-T. *J. Am. Chem. Soc.* **1975**, *97*, 600–610.

[6] See, for example: (a) Acharya, S. P.; Brown, H. C. *J. Chem. Soc., Chem. Commun.* **1968**, 305–306. (b) Fahey, R. C.; McPherson, C. A. *J. Am. Chem. Soc.* **1971**, *93*, 2445–2453. (c) Becker, K. B.; Grob, C. A. *Helv. Chim. Acta* **1973**, *56*, 2723–2732, 2733–2747. (d) Becker, K. B.; Boschung, A. F.; Geisel, M.; Grob, C. A. *Helv. Chim. Acta* **1973**, *56*, 2747–2759. (e) Blunt, J. W.; Coxon, J. M.; Gibson, J. R. *Aust. J. Chem.* **1981**, *34*, 2469–2473.

[7] (a) Dewar, M. J. S.; Fahey, R. C. *J. Am. Chem. Soc.* **1963**, *85*, 2245–2248, 2248–2252. (b) Brown, H. C.; Rei, M.-H. *J. Org. Chem.* **1966**, *31*, 1090–1093.

[8] Consequently, a number of alternative approaches to hydriodination have been developed: (a) Stone, H.; Shechter, H. In *Organic Syntheses*; Rabjohn, N., Ed.; Wiley: New York, 1963; Collect. Vol. IV, pp 543–544. (b) Landini, D.; Rolla, F. *J. Org. Chem.* **1980**, *45*, 3527–3529. (c) Barluenga, J.; González, J. M.; Campos, P. J.; Asensio, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 319–320. (d) Irifune, S.; Kibayashi, T.; Ishii, Y.; Ogawa, M. *Synthesis* **1988**, 366–369. (e) Pagni, R. M.; Kabalka, G. W.; Boothe, R.; Gaetano, K.; Stewart, L. J.; Conaway, R.; Dial, C.; Gray, D.; Larson, S.; Luidhardt, T. *J. Org. Chem.* **1988**, *53*, 4477–4482. (f) Reddy, C. K.; Periasamy, M. *Tetrahedron Lett.* **1990**, *31*, 1919–1920.

[9] See: (a) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; pp 291–296. (b) Stacey, F. W.; Harris, J. F., Jr. *Org. React. (N.Y.)* **1963**, *13*, 150–376.

[10] For a preliminary report, see: Kropp, P. J.; Daus, K. A.; Crawford, S. D.; Tubergen, M. W.; Kepler, K. D.; Craig, S. L.; Wilson, V. P. *J. Am. Chem. Soc.* **1990**, *112*, 7433–7434.

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Table I. Hydrochlorination of Cycloheptene (**1**)[a]

reagent	equiv[c]	adsorbent	surface area, m^2/g	solvent	time, h	yield,[b] % **1**	yield,[b] % **2**
HCl	*d*			CH_2Cl_2	1	94	
HCl	*e*			CH_2Cl_2	1	97	
HCl	*f*	SiO_2[g]	675	CH_2Cl_2	1	3	62
$SOCl_2$	2	SiO_2[h]	500	CH_2Cl_2	4	2	75
$SOCl_2$	2	SiO_2[g]	675	CH_2Cl_2	1	3	81
$SOCl_2$	2	SiO_2[g,i]	675	CH_2Cl_2	1	20	59
$SOCl_2$	2	SiO_2[g,j]	675	CH_2Cl_2	1		77
$SOCl_2$	2	SiO_2[g,k]	675	CH_2Cl_2	1	5	68
$SOCl_2$	2	SiO_2[g]	675	$(C_2H_5)_2O$	2	100	
$SOCl_2$	2	SiO_2[l]	750	CH_2Cl_2	0.3	1	71
$SOCl_2$	2	Al_2O_3	210	CH_2Cl_2	0.3		94
$SOCl_2$	2	Al_2O_3[i]	210	CH_2Cl_2	0.3	8	74
$SOCl_2$	2	Al_2O_3	210	$(C_2H_5)_2O$	2[m]	92	

[a] Conducted according to the standard small-scale procedure described in the Experimental Section with adsorbent that had been equilibrated with the atmosphere at 120 °C for at least 48 h, unless otherwise indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[**1**]. [d] Gaseous HCl was bubbled continuously through the solution at 25 °C. [e] Gaseous HCl was bubbled continuously through the solution at −78 °C. [f] Silica gel added to the preceding solution after 1 h. [g] Merck grade 40. [h] Merck grade 60. [i] 2% (w/w) H_2O added. [j] Dried at 250 °C (0.5 mmHg) for 20 h. [k] Dried at 390 °C (0.5 mmHg) for 20 h. [l] Fisher S157. [m] After 2 h, 5 mL of 2-propanol was added to the reaction mixture, and stirring was continued for an additional 0.5 h. No sulfite **3** was observed.

Table II. Hydrochlorination of Cycloheptene (**1**) with Fumed Silica and Silica Gel[a]

adsorbent	weight, g	surface area, m^2/g	yield,[b] % **1**	yield,[b] % **2**
Cab-O-Sil[c]	1.0	200	92	8
Merck grade 40	1.0	675	39	61
Merck grade 40	0.3	675	65	30

[a] Conducted for 8 h with 2 equiv of $SOCl_2$ according to the standard small-scale procedure described in the Experimental Section, except as indicated above and with 20 mL of CH_2Cl_2 to facilitate stirring. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] Fumed silica.

Table III. Hydrochlorination of α-Pinene (**5**)[a]

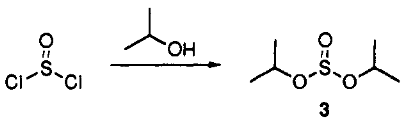
reagent	equiv[c]	adsorbent	solvent	time, min	yield,[b] % **4**	yield,[b] % **5**	yield,[b] % **6**
HCl	2[d]		CH_2Cl_2	15	33	55	8
HCl	2[d]		$(C_2H_5)_2O$	240	96	3	
$SOCl_2$	1	SiO_2	CH_2Cl_2	15		50	3[e]
$SOCl_2$	2	SiO_2[f]	CH_2Cl_2	60		54	8[g]
$SOCl_2$	1	SiO_2	$(C_2H_5)_2O$	15		67	7[e]

[a] Conducted according to the standard small-scale procedure described in the Experimental Section. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[**5**]. [d] Generated in situ by the addition of 1 equiv of $SOCl_2$ and 1 equiv of H_2O. [e] Limonene also obtained in 6% yield. [f] Cab-O-Sil fumed silica (0.25 g). [g] Limonene also obtained in 11% yield.

gave results indistinguishable from those obtained with fresh adsorbent.

The best results were obtained when the adsorbents were equilibrated with moisture in the atmosphere at 120 °C for at least 48 h prior to use. Addition of 2% (w/w) water to silica gel or alumina that had been equilibrated in this way resulted in somewhat slower rates of addition and lower material balances. Poorer results were also obtained with silica gel that had been dried at 250 or 390 °C. A comparison of three grades of silica gel showed that addition occurred more rapidly with increasing surface area. In contrast with silica gel, fumed silica was ineffective in promoting the addition of HCl (Table II).[11]

In contrast with CH_2Cl_2, no reaction occurred with ether as the solvent over either silica gel or alumina (Table I). In principle, the absence of reaction could be due to a lack of hydrolysis of $SOCl_2$ to generate HCl or to a lack of mediation of the addition process. However, addition of 2-propanol to the reaction mixture over alumina failed to give any of the sulfite ester **3**, indicating the absence of remaining $SOCl_2$. Moreover, treatment of α-pinene (**4**) with silica gel in the presence of $SOCl_2$ readily afforded a mixture of adducts **5** and **6** with ether as the solvent (Table III). Being trisubstituted and strained, α-pinene (**4**) is substantially more reactive toward HCl than cycloheptene.[12] Apparently more reactive alkenes are less sensitive to solvent effects on surface-mediated addition. Chlorides **5** and **6** were also formed over fumed silica, showing that the lack of addition to cycloheptene (**1**) over this adsorbent is due to a lack of surface mediation rather than of hydrolysis.



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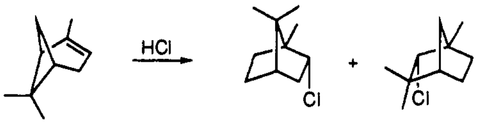
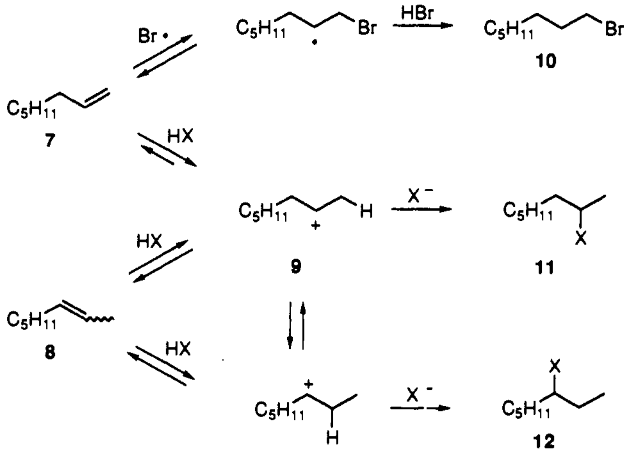


4 **5** **6**

Being only monosubstituted, 1-octene (**7**) also underwent no detectable reaction with HCl in solution, but addition occurred readily in the presence of either silica gel or alumina to afford chloride **11a** (Table IV). This system was used to study the effectiveness of several types of HCl precursors. Treatment of 1-octene (**7**) with $SOCl_2$ or $(COCl)_2$ in the presence of either silica gel or alumina afforded chloride **11a** in good-to-excellent yield. $(CH_3)_3SiCl$ was an effective precursor over alumina but not silica gel. Acetyl chloride gave only slow addition over silica gel and almost no reaction over alumina. Since an almost quantitative yield of chloride **11a** was obtained in a short time over alumina with $(COCl)_2$, this combination is the method of choice.

The amount of HCl precursor used affected the rate of formation and the yield of chloride **11a**. The use of 0.5 mmol of $(COCl)_2$, which would afford 1 mol equiv of HCl under the

Scheme I



a, X = Cl; **b**, X = Br; **c**, X = I

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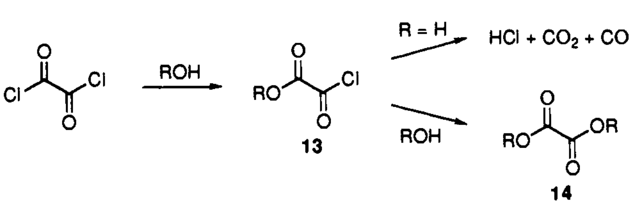
(11) Because of the lower density of fumed silica, it was necessary to use a much lower ratio of adsorbent to alkene. However, silica gel afforded substantial reaction at this ratio and at an even lower ratio that compensated for the smaller surface area of fumed silica.

Table IV. Hydrochlorination of 1-Octene (**7**)[a]

reagent	equiv[c]	adsorbent	time, h	yield,[b] % **7**	yield,[b] % **11a**[d]
HCl	*e*		1	100	
HCl	*e*	SiO_2	1	14[f]	47
HCl	*e*	Al_2O_3	1	11[f]	60
$SOCl_2$	2	SiO_2	4	6[f]	71
$SOCl_2$	2	Al_2O_3	1	*g*	61
$(COCl)_2$	0.5	SiO_2	24	55[f]	45
$(COCl)_2$	1	SiO_2	24	22[f]	68
$(COCl)_2$	2	SiO_2	24	14[f]	74
$(COCl)_2$[h]	2	SiO_2	24	14[f]	86
$(COCl)_2$[i]	2	SiO_2	24	46[f]	43
$(COCl)_2$	0.5	Al_2O_3	2	98	
$(COCl)_2$	1	Al_2O_3	2	35[f]	47
$(COCl)_2$	2	Al_2O_3	1	2[f]	98
$(COCl)_2$[h]	2	Al_2O_3	1	2[f]	75
$(COCl)_2$[i]	2	Al_2O_3	1	95	5
$(CH_3)_3SiCl$	4	SiO_2	24	88[f]	7
$(CH_3)_3SiCl$	4	Al_2O_3	24	12[f]	83
AcCl	4	SiO_2	10	65[f]	35
AcCl	4	Al_2O_3	10	96	*g*

[a] Conducted with CH_2Cl_2 as the solvent according to the standard small-scale procedure described in the Experimental Section, unless otherwise indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[**7**]. [d] Includes some 3-chlorooctane (**12a**). [e] Gaseous HCl was continuously bubbled through the solution at -78 °C. [f] Includes some (*E*)- and (*Z*)-2-octene (**8**). [g] Trace. [h] Inverse addition: 1-octene (**7**) was added to a suspension of Al_2O_3 in CH_2Cl_2 containing $(COCl)_2$ that had been stirred for 5 min. [i] One equiv of CH_3CO_2H was added prior to the addition of $(COCl)_2$.

standard conditions on total hydrolysis, afforded slow reaction over silica gel. No reaction occurred over alumina, presumably because the basic alumina used neutralizes 1 mol equiv of HCl under these conditions.[13,14] With 1 mmol of $(COCl)_2$ reaction occurred more rapidly over silica gel and even more so over alumina. Even better results were obtained with 2 mmol, a 2:1 molar ratio of $(COCl)_2$ to alkene. Hydrolysis studies showed that this is slightly more $(COCl)_2$ than is hydrolyzed over alumina. Under the standard conditions 1.5 mmol of $SOCl_2$ or $(COCl)_2$ was consumed rapidly over 2.5 g of alumina, followed by slower hydrolysis of an additional 0.3 mmol (Figure 1). Hydrolysis was substantially slower over silica gel, accounting for the longer reaction times required with this adsorbent.[15,16] Hydrolysis of $(COCl)_2$ over silica gel and alumina was accompanied by copious formation of gaseous products, as expected from rapid decomposition of the initially formed half-acid **13** (R = H) to CO_2 and CO.[17,18]



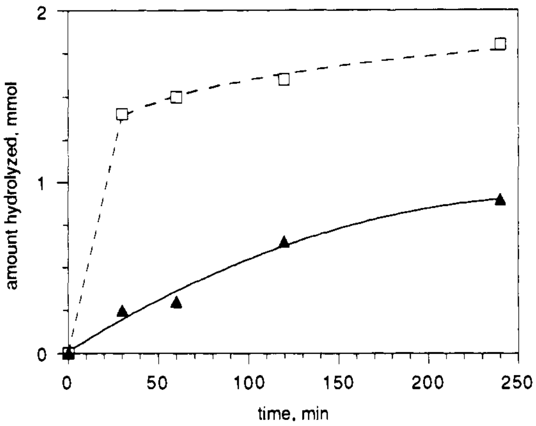


Figure 1. Hydrolysis of 2.0 mmol of $SOCl_2$ and $(COCl)_2$ over 2.5 g of silica gel (▲) and alumina (□).

Table V. Hydrochlorination of 3,3-Dimethyl-1-butene (**15**)[a]

adsorbent	solvent	time, h	relative yield[b] **16**	relative yield[b] **17**
SiO_2	$CHCl_3$	3.5	17	83
SiO_2	C_5H_{12}	4	19	81
Al_2O_3	$CHCl_3$	16	31	69

[a] Conducted according to the standard preparative-scale procedure described in the Experimental Section with 20 mmol of $SOCl_2$. [b] Determined by relative integrations of absorptions at δ 3.90 for chloride **16** and 1.89 for chloride **17** in the product mixture.

The order of addition was found to be important with alumina. The standard procedure, in which $(COCl)_2$ was added to a stirred suspension of alumina in CH_2Cl_2 already containing alkene **7**, gave better results than inverse addition, in which the HCl precursor was added prior to the alkene.[19] On the other hand, silica gel, over which hydrolysis occurs much more slowly, afforded similar results regardless of the order of addition.

In contrast with $SOCl_2$ and $(COCl)_2$, hydrolysis of acetyl chloride was fairly rapid over silica gel, reaching 3.7 mmol after 4 h, but was slower over alumina, reaching only 2.2 mmol after 4 h. The ineffectiveness of acetyl chloride as an HCl precursor in addition reactions is apparently due to the hydrolysis byproduct CH_3CO_2H, since hydrochlorination of 1-octene (**7**) over both silica gel and alumina using $(COCl)_2$ as the HCl precursor was significantly retarded by the inclusion of 1 equiv of CH_3CO_2H. Alumina was particularly deactivated by the presence of CH_3CO_2H.

Rearrangement. When hydrochlorination of 1-octene (**7**) was terminated prior to completion, the remaining alkene contained varying amounts of (*E*)- and (*Z*)-2-octene (**8**). Moreover, chloride **11a** was contaminated with some of the 3-halo isomer **12a**. Thus surface-mediated addition is apparently a stepwise process involving the 2-octyl cation (**9**), which undergoes elimination and rearrangement in competition with nucleophilic trapping (Scheme I).[20] Similarly, α-pinene (**4**) underwent rearrangement to chlorides **5** and **6** (Table III), and 3,3-dimethyl-1-butene (**15**) afforded a mixture of the unrearranged chloride **16** and the rearranged chloride **17** (Table V). Interestingly, the relative

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(12) However, like other alkenes, α-pinene undergoes only slow solution-phase addition in donor solvents such as ether: Hennion, G. F.; Irwin, C. F. *J. Am. Chem. Soc.* **1941**, *63*, 860–862.

(13) Commercially available neutral and acidic alumina exhibit behavior similar to that of basic alumina except that they initially neutralize less of the hydrogen halide.[14]

(14) Kropp, P. J.; Crawford, S. D. Manuscript submitted.

(15) After 24 h, 1.7 mmol of $SOCl_2$ and 0.9 mmol of $(COCl)_2$ had been hydrolyzed over 2.5 g of silica gel. In the presence of excess 2-norbornene (**18**) as an HCl trap, 1.3 mmol of $(COCl)_2$ was hydrolyzed in 24 h. Consistent with the more limited hydrolysis of $(COCl)_2$ over silica gel, better results were generally obtained using $SOCl_2$ rather than $(COCl)_2$ as the HCl precursor with silica gel. On the other hand, $(COCl)_2$ gave better results than $SOCl_2$ with alumina, over which it is extensively hydrolyzed.

(16) Similarly, the ineffectiveness of $(CH_3)_3SiCl$ over SiO_2 is probably due to its very slow hydrolysis over this adsorbent.

(17) Ugi, I.; Beck, F. *Chem. Ber.* **1961**, *94*, 1839–1850.

(18) Hydrolysis of $SOCl_2$ similarly affords the gaseous product SO_2: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980; p 538. However, $SOCl_2$ affords substantially less gas evolution than $(COCl)_2$ on treatment with silica gel or alumina, presumably because of adsorption of SO_2 to the surface.

(19) This is apparently due to the presence of a high concentration of HCl at the time the substrate is added since hydrolysis of $(COCl)_2$ is rapid over alumina. Similarly, surface-mediated addition afforded chlorides in lower yields when a saturated solution of HCl, rather than an HCl precursor, was used.

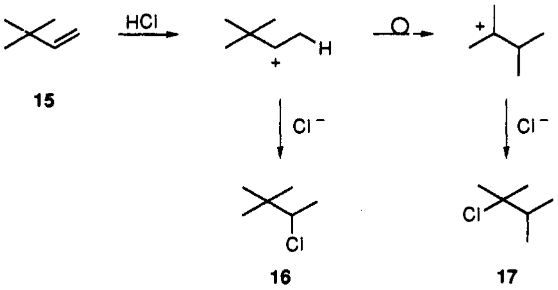
(20) Rearrangement clearly occurs prior to nucleophilic trapping since chloride **12a** was stable under the reaction conditions over both silica gel and alumina.

Table VI. Hydrobromination and Hydriodination of 1-Octene (**7**)[a]

reagent	equiv[c]	adsorbent	time, h	yield,[b] % **7**[d]	**10**	**11**[e]
HBr	*f*		2	50		47
HBr	*g*		0.3	6	83	11
HBr	*g*	SiO_2	0.7	*h*	*h*	96
HBr	*g*	Al_2O_3	0.3			93
$(COBr)_2$	2	SiO_2	1	3		72
$(COBr)_2$	2	Al_2O_3	0.3	1		99
$(CH_3)_3SiBr$	4	SiO_2	2	*h*	9	91
$(CH_3)_3SiBr$	4	Al_2O_3	2	*h*		99
PI_3	0.67	SiO_2	0.3	4		78
PI_3	0.67	Al_2O_3	24	14		85
PI_3	1.0	Al_2O_3	0.3	9		91
$(CH_3)_3SiI$	1.0	SiO_2	1	2		98
$(CH_3)_3SiI$	2.0	Al_2O_3	1	20		80

[a] Conducted according to the standard small-scale procedure described in the Experimental Section, unless otherwise indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[**7**]. [d] Includes some (*E*)- and (*Z*)-2-octene (**8**). [e] Includes some 3-halooctane (**12**). [f] Gaseous HBr was continuously bubbled through the solution at –78 °C. [g] Gaseous HBr was continuously bubbled through the solution at 25 °C. [h] Trace.

amount of rearrangement was the same over silica gel with either $CHCl_3$ or C_5H_{12} as the solvent. On the other hand, more rearrangement occurred over silica gel than alumina.



Hydrobromination. On treatment with HBr in solution at –78 °C, 1-octene (**7**) underwent slow reaction to afford the ionic addition product **11b** (Table VI). Addition occurred more rapidly at 25 °C, but the radical addition product **10** now greatly predominated. However, with silica gel or alumina present under these conditions the ionic product **11b** was formed almost exclusively. Alternatively, bromide **11b** could be easily prepared in high yield by treatment of 1-octene (**7**) with $(COBr)_2$ or $(CH_3)_3SiBr$ as an HBr precursor in the presence of silica gel or alumina. Reaction times were substantially shorter than for hydrochlorination. $(CH_3)_3SiBr$, which undergoes hydrolysis more rapidly than its chloro analog, was effective over silica gel as well as alumina.

Hydriodination. Surface-mediated conditions are also convenient for effecting addition of HI. Thus treatment of 1-octene (**7**) with PI_3 or $(CH_3)_3SiI$ as an HI precursor in the presence of silica gel or alumina readily afforded iodide **11c** (Table VI).

An alternative procedure for hydriodination was recently reported, in which HI is generated in the presence of an alkene by treatment of alumina with I_2.[21] Although this method was found to be effective for the hydriodination of a number of alkenes, the expected adduct **19c** was not obtained from 2-norbornene (**18**), and it was concluded that 2-norbornene (**18**) does not add HI because of steric hindrance. However, this addition occurs readily in solution.[8d,22] Moreover, the situation was found to be no different under surface-mediated conditions since treatment of 2-norbornene (**18**) with PI_3 in the presence of alumina readily afforded iodide **19c** (Table VII). Further investigation of the treatment of 2-norbornene (**18**) with I_2 and alumina revealed that the major product is the diiodide **20**, along with a small amount of iodide **19c**. In contrast with most other alkenes,[23] diiodide formation is irreversible for 2-norbornene (**18**) because of the associated relief of strain, thereby rendering the alkene unavailable for reaction with HI.

Table VII. Hydriodination and Iodination of 2-Norbornene (**18**)[a]

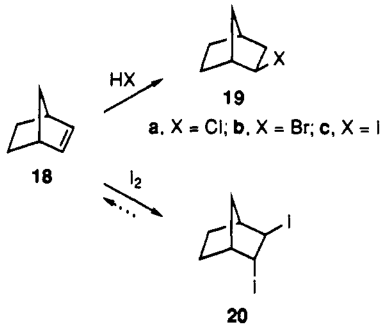
reagent	equiv[c]	adsorbent	solvent	time, h	yield,[b] % **18**	**19**	**20**
PI_3	1.0	Al_2O_3	CH_2Cl_2	0.3		80	
I_2	1.1	Al_2O_3	pet ether[d]	1	2	10	48
I_2	1.1		pet ether[d]	1		*e*	63

[a] Conducted according to the standard small-scale procedure described in the Experimental Section except as indicated. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[**18**]. [d] Conducted under reflux. [e] Trace.

Table VIII. Hydrochlorination of 1-Methylcyclohexene (**21**)[a]

reagent	equiv[c]	adsorbent	time, h	yield,[b] % **21**	**22**
HCl	*d*		1	10	90
$SOCl_2$	2	SiO_2	2	15	67
$SOCl_2$	2	Al_2O_3	2	13	76
AcCl	4	SiO_2	2	10	81
AcCl	4	Al_2O_3	2	59	31

[a] Conducted according to the standard small-scale procedure described in the Experimental Section. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] [Reagent]/[**21**]. [d] Gaseous HCl was continuously bubbled through the solution at –78 °C.



Stereochemistry. Being trisubstituted, 1-methylcyclohexene (**21**) undergoes addition of HCl readily in solution and does not require surface mediation. Nevertheless, use of an HCl precursor such as $SOCl_2$ in conjunction with silica gel or alumina was found to be a convenient method for preparing chloride **22** (Table VIII).[24] Once again, acetyl chloride was an effective precursor with silica gel but not alumina, over which it hydrolyzes more slowly.

The stereochemistry of surface-mediated addition was examined using the tetrasubstituted analog 1,2-dimethylcyclohexene (**24**). In CH_2Cl_2 solution alkene **24** was found to afford a 2.9:1 mixture of chlorides **25c** and **25t**, respectively, which changed little with time.[6b] Both isomers were also obtained on treatment

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(21) Pagni, R. M.; Kabalka, G. W.; Boothe, R.; Gaetano, K.; Stewart, L. J.; Conaway, R.; Dial, C.; Gray, D.; Larson, S.; Luidhardt, T. *J. Org. Chem.* **1988**, *53*, 4477–4482.

(22) (a) Davies, A. G.; Tudor, R. *J. Chem. Soc. B* **1970**, 1815–1818. (b) Kropp, P. J.; Adkins, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 2709–2717.

(23) See, for example: Bowyer, W. J.; Evans, D. H. *J. Electroanal. Chem.* **1988**, *240*, 227–237, and references cited therein.

(24) Subsequent to our preliminary report,[1i] it was reported that treatment of 1-methylcyclohexene (**21**) with $SOCl_2$ both in solution and in the presence of a variety of adsorbents, including silica gel and alumina, afforded mixtures of chloride **22** and the radical addition product **23**: Delaude, L.; Laszlo, P. *Tetrahedron Lett.* **1991**, *32*, 3705–3708. Moreover, silica gel was found to be substantially more effective than alumina in promoting the formation of chloride **22**. Under our conditions there was no detectable formation of chloride **23**, and silica gel and alumina were both effective in promoting the formation of chloride **22**.

Table IX. Treatment of Chlorides **25c** and **25t** over Silica Gel and Alumina[a]

			yield,[b] %					
adsorbent	chloride	time, h	**24**	**25c**	**25t**	**26**	**27**	**25c**/**25t**
SiO_2	**25c**	0		97	3			32
		1	13	19	45			0.42
SiO_2	**25t**	0		7	93			0.1
		1	16	20	49			0.41
SiO_2[c]	**25c**	0		97	3			32
		0.3	84			10		
SiO_2[c]	**25t**	0		7	93			0.1
		2	45	13	5	28		2.6
		4	72	1		27		
Al_2O_3	**25c**	0		91	9			10
		8	10	67	10	6	6	6.7
		24	33	21		19	17	
		48	50			23	20	
Al_2O_3	**25t**	0		2	98			0.02
		8		2	84	5	1	0.02
		24	17		62	17	3	
		48	31		9	27	4	

[a] Conducted according to the standard small-scale procedure for hydrohalogenation described in the Experimental Section except that no HCl precursor was added. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] Four equiv ([**18**]/[**25**]) of 2-norbornene (**18**) was added; chloride **19a** was obtained as an additional product.

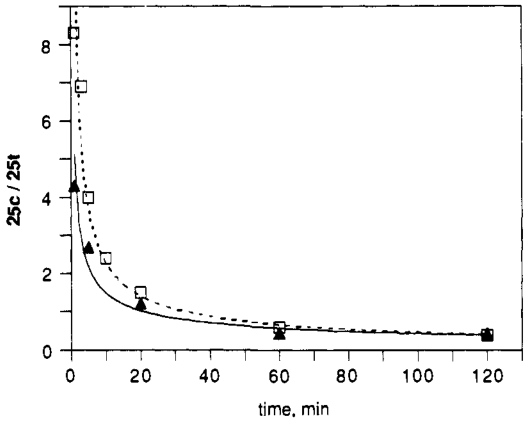
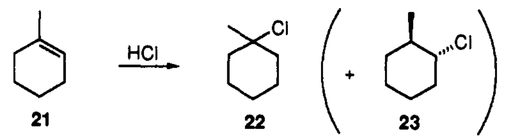
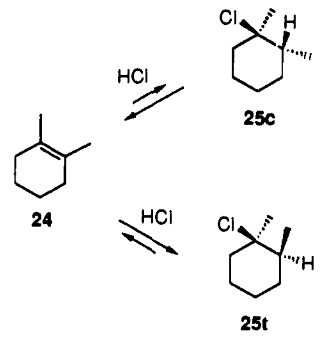


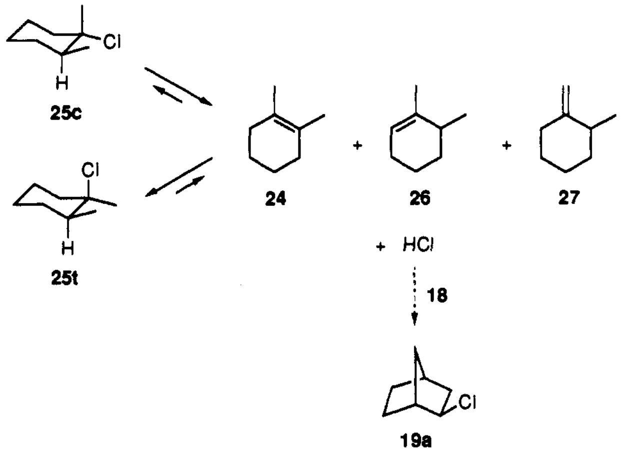
Figure 2. Variation with time of product mixtures from hydrochlorination of 1,2-dimethylcyclohexene (**24**) with 1 equiv of $SOCl_2$ over silica gel (▲) and alumina (□).

of alkene **24** with $SOCl_2$ or $(COCl)_2$ in presence of silica gel or alumina, but their ratio changed rapidly with time (Figure 2). At short reaction times the syn adduct **25c** greatly predominated, whereas at longer times equilibration with the thermodynamically more stable isomer **25t** occurred, ultimately approaching the reported thermodynamic ratio **25c**:**25t** of 0.3.[6c]





The interconversion of chlorides **25c** and **25t** apparently involves reversibility of the addition process. When mixtures of chlorides **25c** and **25t** containing predominantly one or the other isomer were treated with silica gel in the absence of an HCl precursor, rapid equilibration to a **25c**:**25t** ratio of 0.4 occurred, along with the accompanying formation of small amounts of alkene **24** (Table IX). When treatment of chlorides **25c** and **25t** over silica gel was repeated in the presence of 2-norbornene (**18**) as an HCl trap, the syn addition product **25c** rapidly afforded alkene **24**, along with a small amount of the double bond isomer **26**. However, isomer **25t**, which cannot form alkene **24** via syn elimination, underwent reaction much more slowly and afforded substantially more of the double bond isomer **26**, which can be formed via syn elimination.[25] Thus dehydrohalogenation under surface-mediated conditions, like addition, occurs syn.



By contrast, treatment of chlorides **25c** and **25t** over alumina, which neutralizes 1 equiv of acid under the standard conditions and should not require an HCl trap, resulted only in slow, nonselective elimination to a mixture of alkenes **24**, **26**, and **27**. Subsequent studies with chloride **28** revealed that reversal of surface-mediated addition over alumina requires prior treatment with HCl. Chloride **28** underwent rapid elimination to a 5.6:1 mixture of alkenes **29** and **30** over silica gel but slowly afforded a 1.3:1 mixture of alkenes **29** and **30** over alumina. However, pretreatment of the alumina with slightly less than 0.5 equiv of $SOCl_2$ resulted in rapid elimination to alkenes **29** and **30** in the same ratio as was obtained over silica gel. Thus the equivalent

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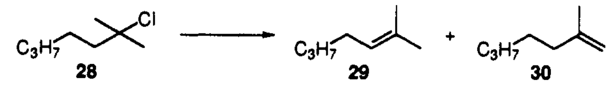
(25) It is likely that alkene **26** is the principal product of elimination from chloride **25t** and that alkene **24** arises via readdition to alkene **26** to afford a mixture of chlorides **25c** and **25t** followed by rapid syn elimination of chloride **25c**.

Table X. Treatment of Chloride **28** over Silica Gel and Alumina[a]

adsorbent	time, h	yield,[b] %			
		28	**29**	**30**	**29/30**
SiO_2[c]	1	10	67	12	5.6
Al_2O_3	48	1	52	39	1.3
Al_2O_3[c,d]	2	12	62	11	5.6

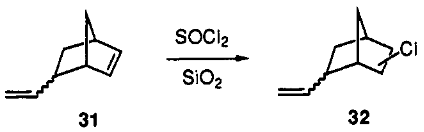
[a] Conducted according to the standard preparative-scale procedure described in the Experimental Section except that no HCl precursor was used. [b] Determined by gas chromatographic analysis relative to an internal hydrocarbon standard on aliquots removed from the reaction mixture. [c] Four equiv ([**18**]/[**28**]) of 2-norbornene (**18**) was added; chloride **19a** was obtained as an additional product. [d] Pretreated with 0.45 equiv of $SOCl_2$ 20 min before the addition of chloride **28**.

of HCl which alumina neutralizes is a prerequisite for surface-mediated addition/elimination with this adsorbent.



28 **29** **30**

Preparative-Scale Reactions. The preceding studies have involved principally a standard small-scale procedure designed to facilitate exploration of a number of aspects of the surface mediation of hydrohalogenations. The procedure was scaled up 20-fold in each case for the isolation and identification of products. To further illustrate the preparative value of the technique, one reaction was conducted on a 160-fold larger scale. Thus hydrochlorination of 5-vinyl-2-norbornene (**31**), which previously required catalysis with $SnCl_4$ and gave only a moderate yield,[26] proceeded rapidly over silica gel with $SOCl_2$ to afford chlorides **32** in 88% yield.

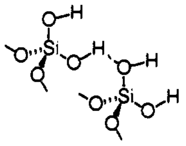


31 **32**

Discussion

Surface Structures. It is thus clear that appropriately prepared surfaces of silica gel and alumina mediate the hydrohalogenation of alkenes and that both the forward and reverse reactions occur in a preferred syn fashion. A key feature of the procedure used in these studies is equilibration of the silica gel or alumina with atmospheric moisture at 120 °C. Silica gel and alumina surfaces that have been so treated are totally hydroxylated, with a small amount of residual physisorbed water.[27,28] The common practice of drying at higher temperatures not only removes the physisorbed water but also changes the structure of the surface through removal of chemisorbed water. Treatment at lower temperatures, or use of the adsorbent out-of-the-bottle, does not ensure total hydroxylation and also may result in the presence of too little or too much physisorbed water, depending on the history of the sample.

Although often referred to as amorphous, the surface of hydroxylated silica gel is microcrystalline, consisting of regions similar to the (100) and (111) faces of β-cristobalite.[29,30] Hydroxylation of the (100) surface affords geminal silanol groups (**33**), which form hydrogen-bonded chains through interaction with neighboring geminal groups, whereas hydroxylation of the (111) surface gives a hexagonal array of isolated silanol groups (**34**) with an O–O distance of 5 Å, well beyond the limit for hydrogen bonding. For silica gel which has been equilibrated at 120 °C, geminal sites constitute about 15% of the total silanol sites.[29] The hydrogen-bonded geminal groups are more acidic (pK_a 5–7) than their isolated counterparts (pK_a 9.5) and are generally regarded as the active sites.[31,32]



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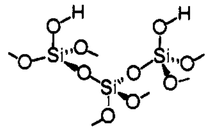

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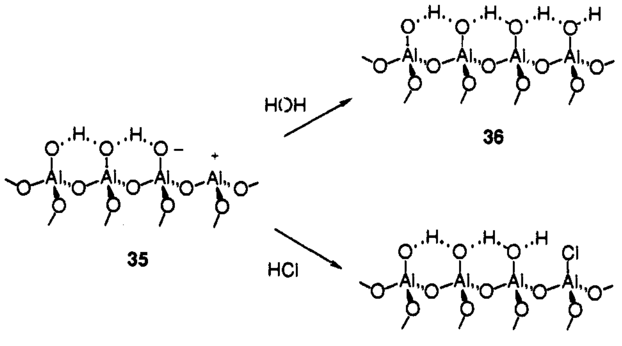

35 **36** **37**

The surface of γ-alumina is similarly heterogeneous, consisting of local regions related to several crystalline faces.[30] Surfaces which have been equilibrated with water vapor at 50–200 °C are generally thought to be terminated by a monolayer of hydroxyl groups separated by about 3.2 Å, within the limit for hydrogen bonding (**36**).[27,33] However, these are apparently not the sites involved in mediating the addition/elimination of hydrogen halides. Although any sites consisting of an oxide ion and adjacent exposed aluminum cation (**35**) that had been previously formed by removal of chemisorbed water on activation at temperatures above 200 °C are generally thought to be rehydroxylated on reexposure to water above 50 °C, the fact that alumina so treated is still basic suggests that some such sites, perhaps highly hindered, remain. It is apparently neutralization of these by the hydrogen halide (**37**) that produces the active sites for addition/elimination.[34]

Mechanism of Addition/Elimination. Hydrogen halides are readily adsorbed from CH_2Cl_2 solution by silica gel and alumina[14] through a hydrogen-bonding interaction, in which acidic OH groups on the surface serve as hydrogen-bond donors (Scheme II).[27,35] Adsorption disrupts any aggregation that the acid had in solution and greatly enhances its acidity through polarization of the H–X bond, leading to protonation of the alkene from the surface.[36,37] Transfer of the halide ion from the surface is apparently rapid, competing with diffusion and affording pre-

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(26) Shields, T. C. *Can. J. Chem.* **1971**, *49*, 1142–1146.

(27) For a review of the surface structure of silica gel and alumina, see: Knözinger, H. In *The Hydrogen Bond. III. Dynamics, Thermodynamics and Special Systems*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Chapter 27.

(28) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1983**, *87*, 5516–5521.

(29) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 1487–1493.

(30) For a recent description of current models for the surfaces of silica gel and alumina, see: Dufour, P.; Houtman, C.; Santini, C. C.; Nédez, C.; Basset, J. M.; Hsu, L. Y.; Shore, S. G. *J. Am. Chem. Soc.* **1992**, *114*, 4248–4257.

(31) For evidence that the most reactive sites are those possessing at least three mutually hydrogen-bonded hydroxyl groups, see: Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931–1936.

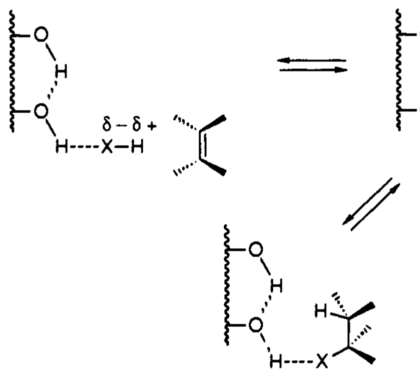
(32) By contrast, fumed silica, which does not mediate hydrohalogenation, has only isolated silanol groups.

(33) The Al–O bonds of alumina are more ionic than the Si–O bonds of silica gel (63% vs 50% on the Pauling scale). Aluminum occupies both tetrahedrally and octahedrally coordinated sites in γ-alumina.

(34) Adsorption of HCl on γ-alumina at room temperature has been shown to form hydroxyl groups from oxide ions and attach chloride ions at adjoining vacant sites: Peri, J. B. *J. Phys. Chem.* **1966**, *70*, 1482–1491. The chlorine atoms undoubtedly enhance the acidity of adjacent hydroxyl groups.

(35) For a similar interaction of triphenylmethyl halides with silica gel, which leads to their ionization, see: Ulbricht, A.; Spange, S.; Heublein, G. *J. Prak. Chem.* **1988**, *330*, 235–240.

Scheme II



dominantly the syn addition product.[38,39] The initially formed cation can undergo competing rearrangement or deprotonation—as seen in the formation of the rearranged chlorides **5** and **6** from α-pinene (**4**), chloride **17** from 3,3-dimethyl-1-butene (**15**), and halides **12**, along with 2-octene (**8**), from 1-octene (**7**).[40] Thus addition, though syn, occurs stepwise. The slower formation of the anti addition product **25t** from 1,2-dimethylcyclohexene (**24**) apparently involves some transfer of chloride ion that occurs after the cationic intermediate has diffused from its initial position, affording a mixture of chlorides **25c** and **25t**. Since addition is reversible under surface-mediated conditions, the mixture of chlorides **25c** and **25t** assumes the thermodynamic ratio with time.

In the absence of the reactive sites required for surface-mediated addition/elimination that are generated on neutralization with HCl, alumina appears to effect slow E2 elimination. The residual basic sites are apparently hindered, since substantial amounts of the less highly substituted alkenes **27** and **30** were formed from chlorides **25** and **28**, respectively.

The deleterious effect of having CH_3CO_2H or excess physisorbed water present is presumably due to competition with the hydrogen halide for hydrogen bonding sites on the surface. Although highly reactive alkenes are capable of adding HCl in solution,[5-7] they presumably undergo primarily surface-mediated addition in the presence of silica gel or alumina because of the rapid adsorption of hydrogen halides onto the surface. This is confirmed by the strong predominance of syn addition of HCl to 1,2-dimethylcyclohexene (**24**) over silica gel and alumina.[41] Similarly, although the stronger acids HBr and HI can add even to the less reactive alkenes in solution, addition is apparently again surface-mediated in the presence of silica gel or alumina. In the case of HBr, adsorption to the surface not only facilitates ionic addition but also renders the polarized HBr unavailable for competing radical addition, affording a simple means of preventing the latter pathway.[42]

Hydrolysis. A second role of silica gel and alumina is effecting hydrolysis of the HX precursor. In principle the formation of HX might involve reaction of the precursor with residual water physisorbed to the surface or with hydroxyl groups on the surface itself. Since silica gel and alumina equilibrated with atmospheric moisture at 120 °C retain some physisorbed water,[27,28,30] it is likely that hydrolysis generally involves first any available water, followed by slower reaction with hydroxyl groups on the surface. This is consistent with the observation of two rates of hydrolysis over alumina. The generally slower hydrolysis over silica gel compared with alumina may be due to the retention of less physisorbed water on silica gel or to slower reaction with the surface.[43]

Concluding Remarks. The use of silica gel and alumina provides a simple means for facilitating additions of HCl which do not occur readily in solution. The results are generally superior to those obtained previously using Lewis acid catalysts, and there is no need to dispose of metal salts. Moreover, the silica gel or alumina can be easily recycled. Even for additions that readily occur in solution, the surface-mediated technique is highly useful. Addition occurs stereoselectively in a syn fashion. In the case of hydrobromination, the use of surface-mediated conditions is a simple means of preventing competing radical addition. Finally, the use of various HX precursors in conjunction with silica gel and alumina eluminates the need to prepare or transfer these corrosive, hygroscopic gases. We continue to explore the rich potential of surface-mediated reactivity.

Experimental Section

General Procedures. All reactions were carried out in oven-dried glassware. Reagents were from commercial suppliers and used without further purification. Gas chromatographic analyses were performed with 3 m × 3 mm stainless steel columns and preparative gas chromatography with 3 m × 6 mm columns packed with (A) 20% SF-96 or (B) 20% Carbowax 20M on 60–80 mesh Chromosorb W or (C) 20% OV-225 on 60–80 mesh Chromosorb P treated with hexamethyldisilizane. Infrared spectra were obtained on neat samples. Nuclear magnetic resonance spectra were recorded in $CDCl_3$ solution at 400 MHz (^1H) or 100 MHz (^{13}C). Melting points are uncorrected.

Surface-Mediated Hydrohalogenations. A. Standard Small-Scale Procedure. Into a 25-mL round-bottomed flask was weighed 2.5 g of Merck 10181 (grade 40) silica gel or Fisher A540 alumina, which had been equilibrated with the atmosphere at 120 °C for at least 48 h. The flask was stoppered, and the contents were allowed to cool to 25 °C. A solution containing 1.0 mmol of the substrate and 0.1 mL of a hydrocarbon internal standard in 5 mL of CH_2Cl_2 was then added. The resulting suspension was stirred, and the indicated amount of HX precursor was added. (CAUTION: vigorous gas evolution when $(COCl)_2$ is added to alumina.) Periodically, 0.2-mL aliquots were removed from the reaction mixture and added to a vial containing 1 mL each of 5% Na_2CO_3 solution and CH_2Cl_2. The vial was shaken, and, upon separation, the organic layer was removed, dried over anhydrous Na_2SO_4, and analyzed by gas chromatography.

B. Standard Preparative-Scale Procedure. Into a 250-mL round-bottomed flask was weighed 25 g of Merck 10181 (grade 40) silica gel or Fisher A540 alumina, which had been equilibrated with the atmosphere at 120 °C for at least 48 h. The flask was stoppered, and the contents allowed to cool to 25 °C. A solution containing 20 mmol of the substrate in 50 mL of CH_2Cl_2 was then added. The resulting suspension was stirred, and the indicated amount of HX precursor was added dropwise as a 1.0 M solution in CH_2Cl_2 over a 20-min period. After continued stirring for the indicated amount of time, the suspension was filtered, and the filtrate was washed with three 25-mL portions of CH_2Cl_2. The combined organic fractions were washed with two 50-mL portions of saturated Na_2CO_3 solution and one of water. The combined aqueous washings were back-extracted with 50 mL of CH_2Cl_2, and the combined organic fractions were dried over saturated NaCl solution followed by anhydrous Na_2SO_4 and concentrated by rotary evaporation or distillation.

C. Procedure for Recycling the Adsorbent. The recovered silica gel or alumina was washed with three 25-mL portions of water followed by three 50-mL portions of acetone, air-dried under suction for 1 h, allowed to stand at 25 °C overnight, and equilibrated with the atmosphere at 120 °C for at least 48 h.

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(36) The surface also provides an exceptionally polar local environment. See: (a) Lindley, S. M.; Flowers, C. G.; Leffler, J. E. *J. Org. Chem.* **1985**, *50*, 607–610. (b) Spange, S.; Keutel, D.; Simon, F. *J. Chim. Phys.* **1992**, *89*, 1615–1622.

(37) It is not clear what role, if any, is played by adsorption of the alkene to the surface. This question is currently under study.

(38) A similar mechanism has recently been proposed for the reaction of gaseous HCl and 1,3-butadiene catalyzed by glass surfaces: Mascavage, L. M.; Chi, H.; La, S.; Dalton, D. R. *J. Org. Chem.* **1991**, *56*, 595–601.

(39) Surface-mediated addition to alkynes also occurs selectively syn.[10,14]

(40) It is interesting that the ratio of unrearranged chloride **16** to rearranged chloride **17** obtained from 3,3-dimethyl-1-butene (**15**) over silica gel is identical with that obtained from the (very slow) solution-phase addition of HCl to alkene **15** in the polar medium CH_3NO_2.[4d] The reason for less rearrangement occurring over alumina is under further study.

(41) Also the highly reactive α-pinene underwent more rapid addition of HCl in CH_2Cl_2 solution in the presence of silica gel.

(42) For a recent application of this based on our preliminary report,[10] see: Walborsky, H. M.; Topolski, M. *J. Am. Chem. Soc.* **1992**, *114*, 3455–3459.

(43) The OH groups on silica are substantially less nucleophilic than those on γ-alumina because of the lower ionic character of the Si–O bond.

Chlorocycloheptane (2). A 1.2-g (10-mmol) portion of $SOCl_2$ was added with stirring to a solution of 0.48 g (5.0 mmol) of cycloheptene (**1**) in 25 mL of CH_2Cl_2 containing 3.0 g of silica gel. The silica gel turned orange-red immediately. Gas chromatographic analysis after 100 min revealed the presence of a single product and only a trace of starting material. Workup as described above and isolation by preparative gas chromatography afforded 0.53 g (80% yield) of chloride **2** as a pale yellow liquid, which was identified by comparison of its gas chromatographic retention time and ^{1}H NMR spectrum with those of a commercial specimen.

Hydrochlorination of α-Pinene (4). Treatment of 3.2 mL (20 mmol) of α-pinene (**4**) with 5.7 mL (80 mmol) of acetyl chloride for 30 min according to the standard preparative procedure followed by preparative gas chromatography (column B) afforded three products. *endo*-2-Chloro-1,7,7-trimethylbicyclo[2.2.1]heptane (**5**) and limonene were isolated as a colorless solid and liquid, respectively, that were identified by comparison of their ^{1}H NMR spectra and gas chromatographic retention times with those of commercial specimens.

endo-2-Chloro-1,3,3-trimethylbicyclo[2.2.1]heptane (**6**) was isolated as a colorless liquid: ^{1}H NMR δ 3.62 (d, J = 2.3 Hz, 1 H, CH-2x), 2.5 (m, 7 H), 1.11 (s, 3 H, CH_3-1), 1.04 (s, 3 H, CH_3-3x), 0.97 (s, 3 H, CH_3-3n); ^{13}C NMR δ 78.68, 47.90, 42.08, 30.62, 26.68, 25.96, 23.49, 19.71; lit.[44] ^{1}H NMR (CCl_4) δ 3.40 (1 H), 1.15 (3 H), 1.08 (3 H), 1.05 (3 H).

1-Bromooctane (10). Treatment of 2.24 g (20.0 mmol) of 1-octene (**7**) with a saturated solution of HBr in CH_2Cl_2 followed by workup in the usual way and isolation by preparative gas chromatography afforded bromide **10** as a colorless liquid that was identified by comparison of its IR spectrum and gas chromatographic retention time with those of a commercial specimen.

2-Chlorooctane (11a). A, Preparation. Treatment of 2.24 g (20.0 mmol) of 1-octene (**7**) with 3.17 g (25.0 mmol) of $(COCl)_2$ and 25 g of alumina according to the standard preparative procedure for 3 h followed by distillation at 40–41 °C (6.5 mmHg) afforded 1.84 g (62% yield) of a colorless liquid that was identified as chloride **11a** containing a minor amount of 3-chlorooctane (**12a**) by comparison of its ^{1}H NMR spectrum with those of commercial specimens.

B, Control Study. Treatment of 1.00 mmol of chloride **11a** with 2.0 equiv of $(COCl)_2$ for 24 h over silica gel or 2 h over alumina according to the standard small scale procedure followed by filtration and rotary evaporation afforded only unchanged chloride as determined by ^{1}H NMR analysis.

2-Bromooctane (11b). Treatment of 1.12 g (10.0 mmol) of 1-octene (**7**) with 4.34 g (20.1 mmol) of $(COBr)_2$ and 12.5 g of alumina according to the standard preparative procedure for 1 h followed by distillation at 72.5–75.0 °C (8.1 mmHg) afforded 1.31 g (68% yield) of a colorless liquid that was identified as bromide **11b** containing a minor amount of 3-bromooctane (**12b**) by comparison of its ^{1}H NMR spectrum with those of commercial specimens.

2-Iodooctane (11c). Treatment of 1.10 g (9.9 mmol) of 1-octene (**7**) with 2.76 g (6.71 mmol) of PI_3 and 12.5 g of silica gel according to the standard preparative procedure for 1.5 h followed by chromatography of the crude product over silica gel afforded, on elution with hexanes, 1.95 g (81% yield) of a colorless liquid that was identified as iodide **11c** containing a minor amount of 3-iodooctane (**12c**) by comparison of its ^{1}H NMR spectrum with those of commercial specimens.

Hydrochlorination of 3,3-Dimethyl-1-butene (15). Treatment of 1.68 g (20 mmol) of alkene **15** in C_5H_{12} solution over silica gel with 1.46 mL (20 mmol) of $SOCl_2$ for 4 h according to the standard preparative procedure followed by distillation afforded 2.21 g (93% yield) of a 19:81 mixture of 3-chloro-2,2-dimethylbutane (**16**) and 2-chloro-2,3-dimethylbutane (**17**), which exhibited the following spectral data. Chloride **16**: ^{1}H NMR δ 3.90 (q, J = 6.8 Hz, 1 H, CH-2), 1.47 (d, J = 6.8 Hz, 3 H, CH_3-1), 1.00 (s, 9 H, 3 × CH_3–); lit.[4f] ^{1}H NMR δ 3.82 (q, J = 6.6 Hz, 1 H), 1.41 (d, J = 6.6 Hz, 3 H), 0.99 (s, 9 H). Chloride **17**: ^{1}H NMR δ 1.89 (heptet, J = 6.8 Hz, 1 H, CH-3), 1.54 (s, 6 H, 2 × CH_3-), 1.02 (d, J = 6.8 Hz, 6 H, 2 × CH_3-); lit.[4f] ^{1}H NMR δ 1.7 (m, 1 H), 1.49 (s, 6 H), 1.00 (d, J = 6.3 Hz, 6 H).

***exo*-2-Iodobicyclo[2.2.1]heptane (19c).** Treatment of 0.944 g (10.0 mmol) of 2-bicyclo[2.2.1]heptene (**18**) with 2.47 mL (30.0 mmol) of acetyl iodide over 25.0 g of alumina for 2 h according to the standard procedure followed distillation from KOH pellets at 40–41 °C (0.80 mmHg) afforded 1.57 g (71% yield) of iodide **19c** as a colorless liquid, which had a gas chromatographic retention time and ^{1}H NMR spectrum identical with those of a sample prepared previously.[22b]

(2-*endo*-3-*exo*)-2,3-Diiodobicyclo[2.2.1]heptane (20). A solution of 1.89 g (20.0 mmol) of bicyclo[2.2.1]hept-2-ene (**18**) and 5.92 g (23.3 mmol) of I_2 in 50 mL of petroleum ether was heated under reflux for 3.5 h in a 50-mL round-bottomed flask. After being allowed to cool, the reaction mixture was washed with two 50-mL portions of 10% $NaHSO_3$ and one each of saturated Na_2CO_3 and water. The combined aqueous washings were back-extracted with 50 mL of petroleum ether. The resulting organic phases were combined, dried over saturated NaCl followed by anhydrous Na_2SO_4, and concentrated by rotary evaporation. Chromatography on silica gel afforded 6.05 g (87% yield) of diiodide **20** as a pale pink liquid: ^{1}H NMR δ 2.37 and 2.47 (2 × s, 2 H, CH-1 and -4), 3.94 (dd, J = 3.8, 2.7 Hz, 1 H, CH-3n), 4.53 (dt, J = 3.8, 1.3 Hz, 1 H, CH-2x);[45] lit.[46] ^{1}H NMR δ 2.42 (br m, 2 H), 3.95 (dd, J = 4, 3 Hz, 1 H), 4.54 (br t, J = 4 Hz, 1 H).

1-Chloro-1-methylcyclohexane (22). Into a 200-mL round-bottomed flask was weighed 20 g of silica gel which had been equilibrated at 120 °C for at least 48 h. The flask was stoppered, and the contents were cooled to 25 °C. A solution of 4.81 g (50.0 mmol) of 1-methylcyclohexene (**21**) in 40 mL of CH_2Cl_2 was added, and the resulting slurry was stirred. A 10 M solution of acetyl chloride (7.11 mL, 100 mmol) in CH_2Cl_2 was added over a period of 5 min. After 7.5 h the mixture was filtered. The filtrate was washed with two 50-mL portions of saturated Na_2CO_3 and one of water. The aqueous washings were back-extracted with 50 mL of CH_2Cl_2. The combined organic extracts were dried over saturated NaCl solution followed by anhydrous Na_2SO_4. Distillation at 59.0–60.5 °C (43 mmHg) afforded 4.62 g (70% yield) of chloride **22** as a colorless liquid: IR 2948 (br), 2864, 1448, 1252, 1144, 766, 542 cm^{-1}; ^{1}H NMR δ 1.9 (br d, 2 H), 1.6 (br m, 7 H), 1.58 (s, 3 H, CH_3-), 1.2 (br q, 1 H); ^{13}C NMR δ 72.6, 41.61, 33.53, 25.24, 22.67; lit.[47] ^{1}H NMR (CCl_4) δ 1.70 (s, 3 H).

Hydrochlorination of 1,2-Dimethylcyclohexene (24). Treatment of 2.20 g (20.0 mmol) of alkene **22** with 5.69 mL (80.0 mmol) of acetyl chloride according to the standard procedure followed by distillation from KOH pellets at 97–103 °C (87 mmHg) afforded 1.83 g (62% yield) of a 3:1 mixture of chlorides **25**. Isolation by preparative gas chromatography (column B) afforded ***cis*-1-chloro-1,2-dimethylcyclohexane (25c)** as a colorless liquid: IR 2972, 2954 (sh), 2936 (br), 2856, 1448 (br), 1438, 1374, 1074, 740, 634 cm^{-1}; ^{1}H NMR δ 2.07 (d, J = 2.7 Hz, 1 H), 1.9 (m, 2 H), 1.7 (m, 4 H), 1.45 (s, 3 H, CH_3-1), 1.4 (m, 2 H), 1,2 (m, 1 H), 1.00 (d, J = 6.8 Hz, 3 H, CH_3-2); lit.[6c] IR 750, 643 cm^{-1}; ^{1}H NMR (CS_2) δ 1.05 (d, 3 H), 1.46 (s, 3 H), 1.0–2.1 (m, 9 H); lit.[6b] IR 752 cm^{-1}.

***trans*-1-Chloro-1,2-dimethylcyclohexane (25t)** was obtained as a colorless liquid: IR 2934, 1440, 1374, 1248, 1146, 1136, 818, 730 cm^{-1}; ^{1}H NMR δ 1.98 (br d, J = 13.1 Hz, 1 H), 1.72 (br m, 2 H), 1.52 (s, 3 H, CH_3-1), 1.48 (br m, 1 H), 142 (br m, 3 H), 1.25 (br m, 1 H), 0.96 (m, 3 H, CH_3-2); ^{13}C NMR δ 77.01, 43.06, 32.12, 31.17, 26.32, 22.85, 17.18; lit.[6c] IR 742, 570, 548 cm^{-1}; ^{1}H NMR (CS_2) δ 1.01 (m, 3 H), 1.55 (s, 3 H), 1.0–2.1 (m, 9 H); lit.[6b] IR 741 cm^{-1}.

Dehydrohalogenation of Chlorides 25c and 25t. From the experiments outlined in Table IX alkene **24**, 1,6-dimethylcyclohexene (**26**), and 1-methyl-2-methylenecyclohexane (**27**) were identified by comparison of their gas chromatographic retention times with those of commercial specimens on two columns (A and B).

2-Chloro-2-methylheptane (28). A. Preparation. According to the standard preparative procedure, a solution of 5.45 g (48.6 mmol) of 2-methyl-1-heptene (**30**) in 40 mL of CH_2Cl_2 was added to 20 g of alumina that had been allowed to cool in a 300-mL round-bottomed flask. A solution of 5.46 g (45.9 mmol) of $SOCl_2$ in 6 mL of CH_2Cl_2 was added dropwise with stirring over a 30-min period. The solution refluxed due to the heat generated, and the alumina turned light brown. Stirring was continued overnight. Isolation in the usual way, followed by distillation at 89–93 °C (95 mmHg) afforded 3.05 g (77% yield) of chloride **28** as a colorless liquid: ^{1}H NMR δ 1.7 (m, 2 H), 1.56 (s, 6 H, 2 × CH_3-),

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(45) Weak absorptions at δ 3.93 and 4.52 suggested the presence of 8% of *exo*-2-*anti*-7-diiodobicyclo[2.2.1]heptane as an impurity. There was also trace absorption at δ 3.78 corresponding to 3-iodotricyclo[2.2.1.0^{2,6}]heptane but no detectable absorption corresonding to *exo*-2-*syn*-7-diiodobicyclo[2.2.1]heptane. See ref 46.

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1.5 (m, 2 H), 1.3 (m, 4 H), 1.56 (t, $J = 6.9$ Hz, 3 H, CH_3-7); ^{13}C NMR δ 71.30, 46.09, 32.42, 24.81, 22.58, 14.03; lit.[48] no spectral data.

B. Dehydrohalogenation. From the experiments outlined in Table X, 2-methyl-2-heptene (**29**) and 2-methyl-1-heptene (**30**) were identified by comparison of their gas chromatographic retention times with those of commercial samples.

***exo*-2-Chloro-5(or 6)-ethenylbicyclo[2.2.1]heptane (32).**[49] To a 1-L flask were added 20.1 g (0.167 mol) of 5-ethenylbicyclo[2.2.1]hept-2-ene (**31**), 500 mL of CH_2Cl_2, and 83 g of silica gel. Thionyl chloride (25 mL, 0.34 mol) was slowly added over a 5-min period. After 15 min of stirring, the CH_2Cl_2 solution was washed with three 100-mL portions of saturated $NaHCO_3$ solution and 200 mL of water and then dried over 200 mL of saturated NaCl solution followed by anhydrous Na_2SO_4. Removal of solvent by rotary evaporation followed by distillation gave 23.0 g (88% yield) of chlorides **32** as a colorless liquid: bp 68–70 °C (3.5 mmHg); ^1H NMR δ 5.72 (m, 1 H, -CH=), 5.01 (m, 2 H, $=CH_2$), 3.83 (m, 1 H, CH-2n), 1.7 (m, 9 H); lit.[26] bp 37 °C (1.0 mmHg); ^1H NMR ($CDCl_3$) δ 6.20–4.70 (m, 3 H), 3.80 (m, 1 H), 2.60–0.70 (m, 9 H).

Hydrolysis Studies. A. $SOCl_2$ and $(COCl)_2$. A 2.0-mmol portion of $SOCl_2$ or $(COCl)_2$ was added to a stirred suspension of silica gel or alumina in 5 mL of CH_2Cl_2 containing a hydrocarbon internal standard according to the standard small-scale procedure. At the appropriate time 5 mL of 2-propanol was added, and stirring was continued for an additional 45 min. An aliquot removed from the reaction mixture was then analyzed by gas chromatography (column A) for the bis(1-methylethyl) ester of sulfurous acid (**3**) or ethanedioic acid [**14**, R = $(CH_3)_2CH$]. Isolation by preparative gas chromatography afforded the esters as colorless liquids. Ester **3**: IR 2985, 2940, 1465, 1385, 1205, 1190, 1105, 920, 905, 860, 835, 745 cm^{-1}; ^1H NMR (250 MHz) δ 4.76 (septet, $J = 6.2$ Hz, 2 H), 1.31 (t, $J = 6.0$ Hz, 12 H); ^{13}C NMR (63 MHz) δ 68.2, 23.6; lit.[50] ^1H NMR (CCl_4) δ 4.78 (m, 2 H), 1.34 (d, 12 H). Ester **14** [R = $(CH_3)_2CH$]: IR 3000, 2945, 1765, 1745, 1368, 1315, 1198, 1095, 905, 835 cm^{-1}; ^1H NMR (250 MHz) δ 5.16 (septet, $J = 6.3$ Hz, 2 H), 1.35 (d, $J = 6.3$ Hz, 12 H); ^{13}C NMR ($CDCl_3$) δ 157.5, 70.8, 21.1; lit.[51] ^{13}C NMR (DMSO-d_6) δ 157.3, 70.6, 21.0.

B. Acetyl Chloride. A 2.0-mmol portion of acetyl chloride was added to a stirred suspension of silica gel or alumina in 5 mL of CH_2Cl_2 containing 1,1,2,2-tetrachloroethane as an internal standard according the standard small-scale procedure. Periodically 0.2-mL aliquots were removed from the reaction mixture, diluted to 1 mL with $CDCl_3$, and analyzed by ^1H NMR spectroscopy.

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