of 20 min under a nitrogen atmosphere. After 12 h at 0 °C, water was added, and the organic product was extracted with three portions of tetrahydrofuran and three portions of ether. The solution was dried ($MgSO_4$) and evaporated under reduced pressure to give 1.3 g (67% crude yield) of exo alcohol **40a** as a yellow liquid. An analytical sample was obtained by preparative GC (column C, 140 °C, 85 mL/min, t_R = 14.5 min). The IR and NMR spectral data correspond to those reported in the literature.[24c,33]

***endo*-Bicyclo[4.1.0]heptan-3-ol (40b)** was prepared by Simmons–Smith reaction of 3-cyclohexenol according to the procedure of Hanack and Krause.[24c] The product was removed from unreacted starting material by preparative GC (column C, 140 °C, 85 mL/min, t_R = 15.5 min). The IR and NMR spectral data correspond to those reported in the literature.[24c,33]

(33) Aumelas, A.; Casadevall, E.; Casadevall, A. *Tetrahedron* **1978**, *34*, 2481–90.

Acknowledgment. This research was supported in part by grants (No. 76-07513 and 81-11843) from the National Science Foundation. L.A.L. thanks E. I. du Pont de Nemours and Co. for a fellowship during 1978–1979.

Registry No. **1**, 39095-74-4; **2**, 82149-71-1; **3**, 628-41-1; **4**, 17351-28-9; **5**, 4074-22-0; **6**, 4190-06-1; **7**, 500-23-2; **8**, 111-78-4; **9**, 592-42-7; **10**, 6802-78-4; **11**, 38749-43-8; **12**, 66036-93-9; **13**, 66036-95-1; **14**, 24449-05-6; **15**, 82149-72-2; **16**, 32264-69-0; **17**, 2570-09-4; **18**, 82149-73-3; **19**, 71623-13-7; **20**, 71623-14-8; **21**, 82189-11-5; **22a**, 82149-74-4; **22b**, 82189-12-6; **23a**, 82149-75-5; **23b**, 82189-13-7; **24**, 64836-85-7; **25a**, 82149-76-6; **25b**, 82149-77-7; **26**, 82149-78-8; **27**, 82149-79-9; **28a**, 82149-80-2; **28b**, 82189-14-8; **29**, 82149-81-3; **30a**, 82149-82-4; **30b**, 82189-15-9; **30c**, 82189-16-0; **30d**, 82189-17-1; **31a**, 82149-83-5; **31b**, 82189-18-2; **31c**, 82189-19-3; **31d**, 82189-20-6; **34**, 82149-84-6; **35**, 82149-85-7; **36**, 82149-86-8; **37**, 82149-87-9; **38**, 82149-88-0; **39**, 64836-86-8; **40a**, 70064-28-7; **40b**, 40213-64-7; **41a**, 82149-89-1; **41b**, 78002-56-9; **42**, 51372-02-2; **43**, 82149-90-4; **44**, 33162-94-6; benzene, 71-43-2.

Synthesis of Adamantane Derivatives. 59.[1] Reactions of Some Electrophilic Adamantane Derivatives with Unsaturated Organosilanes

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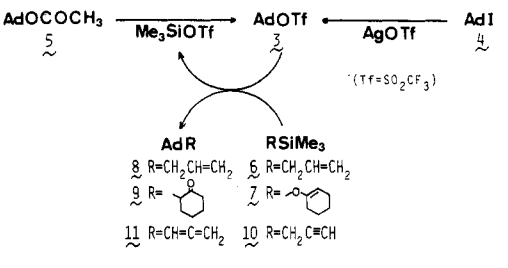
1-Adamantyl acetate (**5**) and 1-adamantyl silyl ether (**12**) react with unsaturated organosilanes exactly as the chloride **1** does; the reactions of **5** catalyzed by trimethylsilyl triflate and of **12** catalyzed by $TiCl_4$ with **6** and **7** give the corresponding adamantane-substituted products. Under $AlCl_3$-catalyzed conditions, the reactions of 1-adamantylcarbinyl chloride (**17**) with **6** and **7** give the products which have a homoadamantane skeleton. Interestingly, the reactions of 1-adamantanecarbonyl chloride (**22**) with α,β- and β,γ-unsaturated silanes proceed smoothly at −78 °C ($TiCl_4$) or at room temperature ($ZnCl_2$) while the competitive decarbonylation scarcely takes place. Furthermore, the reactions of **22** with silyl enol ethers are efficiently catalyzed with normal Lewis acids such as $SnCl_4$ to give C-adamantanecarbonylated products. Some adamantane-substituted unsaturated silanes are acetylated under the conditions employed for **22** to give structurally related adamantane derivatives. The aldehyde (**53**) and ketone (**54**) show different reactivity to the unsaturated organosilanes; the former reacts with **6**, **7**, and **25** as usual, but the latter does not.

The extensive growth of organosilicon chemistry has created a growing awareness of its considerable synthetic utility.[2] In the previous papers,[3] we reported the applicability of unsaturated organosilanes to the synthesis of adamantane derivatives: 1-Adamantyl (=Ad) chloride (**1**) was shown to be reactive with a variety of reagents categorized as X=Y—Z—$SiMe_3$, X≡Y—$SiMe_3$, and X=Y=Z—$SiMe_3$ (X, Y, and Z = C, N, O, and S) in the presence of Lewis acid, wherein the chemical behavior of an adamantyl cation was sometimes different from that of other electrophiles. In the present study we have chosen to examine the reactivity of the electrophiles obtained from adamantane derivatives other than the chloride **1**, i.e., acetate **5** and silyl ether **12** derived from the alcohol **2**, homologous chloride **17**, and carbonyl compounds **22**, **53**, and **54** which are electrophilic at the position adjacent to the bridgehead. Of particular interest is Lewis acid-catalyzed substitution reaction in the case of acid chloride **22** since few successful findings have appeared so far as a result of the intrinsic instability of the carbonyl cation, which tends to undergo decarbonylation. In addition, we have attempted the reactions of adamantane-substituted unsaturated silanes which give the products structurally related to those obtained from **22**.

Scheme I



Results

Reactions of AdOR (R = $COCH_3$, $SiMe_3$). Although **1** is a straightforward precursor for the bridgehead cation,

(1) Part 58: Sasaki, T.; Nakanishi, A.; Ohno, M. *Chem. Pharm. Bull.* **1982**, *30*, 2051.
(2) (a) Fleming, I. "Comprehensive Organic Chemistry"; Jones, D. N., Ed.; Pergamon Press: New York, 1979; Vol. 3, Chapter 13. (b) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981.
(3) (a) Sasaki, T.; Usuki, A.; Ohno, M. *J. Org. Chem.* **1980**, *45*, 3559. (b) Sasaki, T.; Nakanishi, A.; Ohno, M. *Ibid.* **1981**, *46*, 5445.

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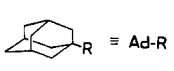
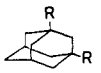
derivatives of alcohol **2** also possibly become its alterna-



≡ Ad-R



1, R = Cl
2, R = OH
12, R = $OSiMe_3$
58, R = SO_2Cl
59, R = $SO_2CH_2CH{=}CH_2$
60, R = $N(Cl)CH_3$
61, R = $N(Cl)COCH_3$
62, R = N_3

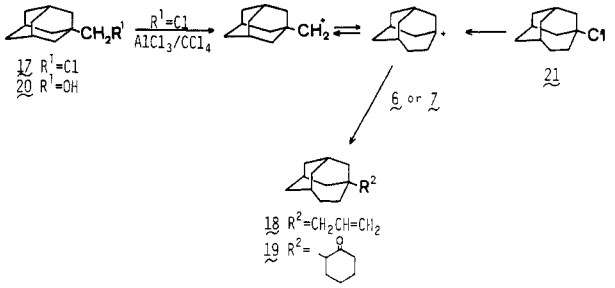
13, R = Cl
14, R = $CH_2CH{=}CH_2$
15, R = OH
16, R = $OSiMe_3$

tives. 1-Adamantyl trifluoromethane, sulfonate (triflate, **3** prepared in situ from iodide **4** and silver triflate was found to react even with benzene, indicating its ability to react with more nucleophilic unsaturated silanes. Recently Simchen and Emde reported that action of trimethylsilyl triflate caused dealkylation of *tert*-alkyl acetate.[4] By using this procedure the other chemists reported selective hydrolysis of *tert*-alkyl and benzyl esters, in which the *tert*-butyl triflate formed caused the concomitant elimination reaction. Nevertheless, this sequence is prohibited in 1-adamantyl acetate (**5**)[6a] due to Bredt's rule, and, therefore, **3** is allowed to react in turn with allylsilane **6** and the silyl enol ether of cyclohexanone (**7**) to give 1-allyladamantane (**8**) and 2-(1-adamantyl)cyclohexanone (**9**) in 70% and 43% yields, respectively (Scheme I). In this case silyl triflate can be recycled and thus used in a catalytic amount.[6b] By applying this triflate-catalyzed reaction, (1-adamantyl)allene (**11**) could be obtained from **5** and propargylsilane (**10**) in 46% yield. This triflate as a catalyst for silyl ether **12** was not effective. Instead, $TiCl_4$ accomplished the similar type of substitution reaction with **12**, giving **8** and **9** in 68% and 72% yields, respectively. This type of reaction was utilized in the diallylation. 1,3-Dichloroadamantane (**13**) afforded only a trace of 1,3-diallyladamantane (**14**) under $TiCl_4$- or $AlCl_3$-catalyzed conditions with a prolonged reaction time. In contrast, 1,3-bis[(trimethylsilyl)oxy]adamantane (**16**) led to the formation of **14** within 15 min at −78 °C. Such a reactivity difference may come from a "cage effect", characterized by an adamantane skeleton;[7] the bridgehead cation first formed in **13** may be destabilized but not that in **16**. These results demonstrate that derivatives of alcohols (**5** and **12**) can be substituted for the chloride **1**, and **16** gives better results than the dichloride **13**. The analogous alkylation was communicated recently by use of acetate and zinc iodide as a catalyst.[8]

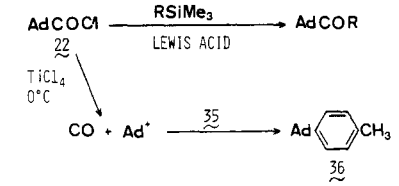
Reactions of AdC(=X)R (X = H_2, R = Cl; X = O, R = Cl, H, CH_3). Next attempted were the electrophilic substitution reactions of adamantane derivatives at the adjacent position to the bridgehead.

1-Adamantylcarbinyl chloride (**17**) was treated with **6** at 0 °C in the presence of $TiCl_4$ in $CHCl_3$ (Scheme II); the reaction was very sluggish, resulting in the recovery of more than half of the starting chloride. The catalyst was then changed to $AlCl_3$, and thereby **17** was actually consumed, but no allylation products were obtained. Consequently,

Scheme II



Scheme III



the substitution reaction took place when CCl_4 was used as a solvent with $AlCl_3$, giving rearranged 3-allylhomoadamantane (**18**) in 74% yield. This result seems to be reasonable because an equilibrated homoadamantyl cation leading to **18** is preferred to an adamantylcarbinyl cation under kinetic control,[9] and, moreover, no primary carbocation is precedented to react with unsaturated organosilanes. In contrast, the $AlCl_3$-catalyzed reaction of **17** with benzene carried out under thermodynamic control (80 °C) is reported to give 1-benzyladamantane.[9] Accordingly, the same yield was obtained even by using a mixture of chloride **17** and **21**, which often has been produced in the chlorination (for example, a 36:67 mixture from the reaction of **20** and thionyl chloride–pyridine). The rearranged structure for **18** was easily deduced by NMR analyses; the ^1H NMR spectrum showed a doublet signal at δ 1.91 due to an allylic methylene, and the decoupled ^{13}C NMR spectrum showed eight peaks at δ 27.9, 31.7, 33.2, 36.4, 36.9, 38.0, and 43.9, assignable to homoadamantane ring carbons. Under the same conditions, **19** was obtained from **7** in 65% yield.

1-Adamantanecarbonyl chloride (**22**) usually undergoes the catalytic Friedel–Crafts-type of reaction with difficulty, because the intermediate complex of **22** with Lewis acid readily decarbonylates; the $AlCl_3$-catalyzed reaction of **22** with benzene was shown to give only 1-phenyladamantane.[10] Successful adamantanecarbonylation toward acetylenes was reported under nonnucleophilic conditions with adamantanecarbonyl tetrafluoroborate or hexafluoroantimonate.[11] We found that **22** reacted smoothly with a variety of unsaturated organosilanes at −78 °C in the presence of $TiCl_4$ or at room temperature in the presence of $ZnCl_2$ without appreciable decarbon-

(4) Emde, M.; Simchen, G. *Synthesis* **1977**, 867.
(5) Borgulya, J.; Bernauer, K. *Synthesis* **1980**, 545.
(6) (a) 1-Adamantyl trifluoroacetate might be a useful ester for this purpose because it is prepared directly from adamantane itself (Jones, S. R.; Mellor, J. M. *J. Chem. Soc. Perkin Trans 1* **1976**, 2576), but no reaction took place. (b) For this type of catalyzed reaction with acetals see: Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1979**, 4679. Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248.
(7) Fort, R. C., Jr. "Adamantane"; Marcel Dekker: New York, 1976; p 161.
(8) Reetz, M. T.; Huettenhain, S.; Huebner, F. *Synth. Commun.* **1981**, *11*, 217.
(9) Margosian, D.; Speier, J.; Kovacic, P. *J. Org. Chem.* **1981**, *46*, 1346. These authors indicated that **17** and **21** involve a common intermediate like a weakly bridged cation in the presence of $AlCl_3$. We believe that such a homoadamantyl cation must likewise be involved in this reaction, though in the absence of substrates, the definite $AlCl_3$-catalyzed preequilibrium **17** ⇄ **21** could not be observed because of side reactions (polyhalogenation?).
(10) Stetter, H.; Rauscher, E. *Chem. Ber.* **1960**, *93*, 1161. For a ^1H NMR study of this type of complex see: Olah, G. A.; Comisarow, M. B. *J. Am. Chem. Soc.* **1966**, *88*, 4442. However, the reported acylations of *p*-anisole with bi- and tricyclic acyl chlorides including **22** indicate that **22** can react as an acylating agent prior to decarbonylation with electron-affluent aromatic and olefinic substrates: Pratt, D. G.; Rothstein, E. *J. Chem. Soc. C* **1968**, 2548.
(11) Kanishev, M. I.; Schegolev, A. A.; Smit, W. A.; Caple, R.; Kelner, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 5660.

ylation. The present success may be due to the enhanced nucleophilicity of silylated olefins and the inertness of the formed trimethylsilyl chloride.

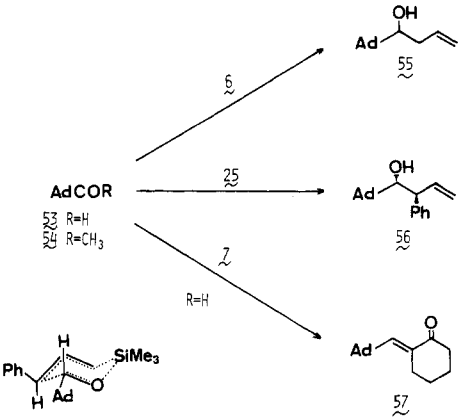
Thus the reaction of **22** carried out with **6** afforded 1-adamantyl allyl ketone (**23**) in 70% yield with $TiCl_4$ at −78 °C for 5 h or in 78% yield with $ZnCl_2$ at room temperature for 14 h. Similarly, cyclic silane **24** and cinnamylsilane (**25**) yielded the expected products **26** and **27**, respectively; **27** is a regiospecific product due to direction by a silyl group rather than a phenyl group. Although the attempted reaction with vinyltrimethylsilane (**28**) failed, analogous silanes were satisfactory; the similar treatment of **22** with phenylethynyl-, furyl- and thienylsilanes **29–31** gave the corresponding ketones (**32–34**, respectively). Exceptionally, *o*-(trimethylsilyl)toluene (**35**) did not show appreciable reactivity under the $TiCl_4$-catalyzed conditions at −78 °C and resulted in the formation of *p*-(1-adamantyl)toluene (**36**) due to the preferential decarbonylation at 0 °C (Scheme III); we have already proved that an adamantyl cation gave rise to **36** with **35**.[3a]

The reactions of **22** with silyl enol ethers are noteworthy. Active acyl halides such as polyhalogenated acid chlorides,[12a] oxalyl chloride,[12b] and acyl tetrafluoroborate[12c] are reported to react smoothly with silyl enol ethers under mild conditions. Also, with silyl ketene acetals, even simple acyl halides were shown to react in the absence or presence of a catalyst (e.g., trimethylamine or zinc halide).[12d] In these reactions C-acylation was observed. On the other hand, simple acyl halides resist reaction with typical silyl enol ethers and hence need a catalyst; however, they do not always give C-acylation products. With mercury(II) chloride as the catalyst, O-acylated products were obtained.[12e] This is not the case when a Lewis acid other than a mercury(II) salt is employed. We found that **22** underwent straightforward C-adamantanecarbonylation with silyl enol ethers, catalyzed by normal Lewis acids such as $TiCl_4$ or $SnCl_4$ (in general $SnCl_4$ was a better catalyst). Thus we could obtain 2-[(1-adamantyl)carbonyl]cyclohexanone (**37**) and -cyclopentanone (**39**) in 65% yield ($SnCl_4$) at −78 °C for 8 h. Similarly, β-diketones **41** and **43** and β-keto aldehyde **45** were prepared from **40**, **42**, and **44**, respectively. Within the limit of NMR analysis, the structure of these dicarbonyls leans one-sidedly to a keto form for **37** and **39** and to an enol form for **41** and **43**. These facts were rationalized by well-known steric and conjugative effects;[13] an adamantyl group is one of the bulkiest groups. Under the conditions employed for **22**, structurally related ketones **49–51** were obtained by acylation of adamantane-substituted unsaturated silanes **46–48** with acetyl chloride. Symmetrical β-diketone **52** was thus prepared from **22** and **48**.

All of the obtained products showed characteristic carbonyl absorptions in the IR spectra and reasonable signals in the NMR spectra, which are summarized in Table I together with the reaction conditions and the physical data.

Up to this time nucleophilic conditions have been rather preferred for **22**. Nevertheless, the present Lewis acid catalyzed electrophilic substitution reactions of **22** with unsaturated organosilanes can be an alternative method

Scheme IV



for the preparation of various adamantyl ketone derivatives.

Both aldehydes and ketones have been documented to act as electrophiles toward unsaturated organosilanes to give formally Grignard reagent addition type products.[14] Thus we finally attempted the reactions of the corresponding adamantane derivatives **53** and **54**. $TiCl_4$-catalyzed reaction of the aldehyde **53** with **6**, **25**, and **7** in CH_2Cl_2 at 0 °C led to the formation of the expected alcohols **55** and **56** and enone **57**, respectively, albeit in low yields. On the contrary, the ketone **54** showed no appreciable reactivity even when the reaction was conducted at room or reflux temperature where less hindered ketones are reported to react with them.[14] These results suggest that this type of reaction is more sensitive to the steric effect than expected.[15] The structure of **56** was assigned to have a threo form on consideration of the cyclic transition state as shown in Scheme IV in which the bulky adamantyl and phenyl groups should be placed in the equatrial positions. This assignment is supported by the relatively small coupling constant (5 Hz) in its NMR spectrum.

Related substitution reactions in which an electrophilic center is a heteroatom were successful only in the case of adamantanesulfonylation of **6** by **58** to give **59** in 43% yield. We could not identify any products from the $AlCl_3$-catalyzed reactions[16] of chloramines **60** and **61** and azide **62** with **6** and **7**.

Experimental Section

Infrared spectra were determined on a JASCO IRA-1 spectrophotometer. ^1H NMR spectra were determined at 60 MHz in the indicated solvent with a JEOL 60-HL spectrometer. In all spectra, signals due to adamantane ring protons were recognized usually in the δ 1.5–2.2 region as a multiplet. ^{13}C NMR spectra were determined with a JEOL JNM-FX60 spectrometer. Chemical shifts were recorded with tetramethylsilane as an internal standard. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. Melting points were determined on a Yanaco MP apparatus and are uncorrected. All of the chromatographic separations were carried out on a silica gel column (Mallinckrodt, 100 mesh) with the solvent noted. Allyl- and vinylsilane-type of reagents **10**,[17] **24**,[18] **25**,[17] **29**,[17] **30**,[19] and **31**[20]

(12) Review for these reactions: ref 2b, chapter 17. Rasmussen, J. K. *Synthesis* **1977**, 91. (a) Murai, S.; Kuroki, Y.; Hasegawa, K.; Tsutsumi, S. *J. Chem. Soc., Chem. Commun.* **1972**, 946. (b) Murai, S.; Kuroki, Y.; Aya, T.; Sonoda, N.; Tsutsumi, S. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 741. (c) Kopka, I.; Rathke, M. W. *J. Org. Chem.* **1981**, *46*, 3771. (d) Fleming, I.; Goldhill, J.; Paterson, I. *Tetrahedron Lett.* **1979**, 3209 and footnotes 64 and 65 in ref 2b, chapter 17. (e) Kramarova, E. P.; Baukov, Y. I.; Lutsenko, I. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1973**, *45*, 469.

(13) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; p 495.

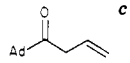
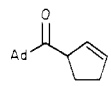
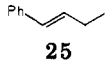
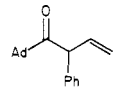
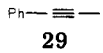
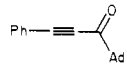
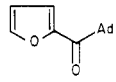
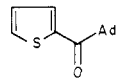
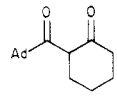
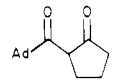
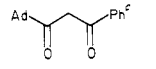
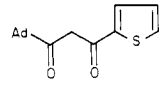
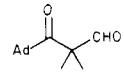
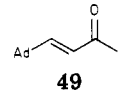
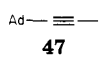
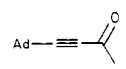
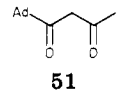
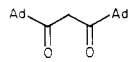
(14) (a) Deleris, G.; Dunogues, J.; Calas, R. *J. Organomet. Chem.* **1975**, *93*, 43. (b) Hosomi, A.; Sakurai, H.; *Tetrahedron Lett.* **1976**, 1295. (c) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503.

(15) We have observed the steric effect due to the adamantane bulkiness in the reactions of **1** with *O*-silyl lactims (see ref 1).

(16) (a) Padeginas, S. J.; Kovacic, P. *J. Org. Chem.* **1972**, *37*, 2672. (b) Sasaki, T.; Eguchi, S.; Kiriyama, T.; Suzuki, H. *Synth. Commun.* **1971**, *1*, 267. (c) Margosian, D.; Kovacic, P. *J. Org. Chem.* **1981**, *46*, 877.

(17) See footnotes 22, 23, and 25 in ref 3a.

Table I. Reactions of 22 with Unsaturated Organosilanes and of Acetyl Chloride with 46-48[a]

R of $RSiMe_3$	reaction conditions[b,d] 1	2	3	product	yield,[d] %; mp, °C	IR, cm^{-1}	^1H NMR (CCl_4), δ
6	Z [T]	rt [−78]	14 [5]	 23	78 [70]; oil	1690, 1640, 990, 910	3.15 (2 H, d, J = 7 Hz, CH_2), 4.7-6.2 (3 H, ABX, vinyl)
 24	T	−78	8	 26	74; 60-63	1690, 1605	3.95 (1 H, m, C_3 H), 4.5-4.8 (2 H, m, CH=CH)
 25	T	−78	3 q	 27	34; 40-43	1695, 1635, 990, 910	4.73 (1 H, d, J = 8 Hz, CHPh), 4.93, 4.98, and 6.06 (each 1 H, ABX, J = 17, 10 Hz and J = 17, 10, 8 Hz, respectively ($CH=CH_2$)
 29	Z	rt	36	 32	40; 68-69	2200, 1655	7.2-7.7 (5 H, m, phenyl)
 30	Z [T]	rt [−78]	50 [8]	 33	61 [13]; 75-77	1655, 1565	6.39, 7.06, and 7.42 (each 1 H, dd, d, and d, J = 2 and 4 Hz, J = 4 Hz, and J = 2 Hz, respectively, furyl)
 31	Z	rt	20	 34	82; 91-92	1630, 1520	6.96, 7.74, and 7.71 (each 1 H, dd, d, and d, J = 3.5 and 4.5 Hz, J = 4.5 Hz, and J = 3.5 Hz, respectively, thienyl)
7	S [T]	−78 [−78]	8 [3]	 37	65 [40]; 85-87	1715, 1680	3.90 (1 H, t, J = 4 Hz, COHCO)
 38	S [T]	−78 [−78]	8 [8]	 39	65 [45]; 100-103	1720, 1695	3.83 (1 H, t, J = 6 Hz, COHCO)
 40	S	−78	8	 41	50; 44-46	1700, 1600	6.11 (1 H, s, CH=C), 7.2-8.0 (5 H, m, phenyl), 16.50 (1 H, s, OH)
 42	S [T]	−78 [−78]	8 [8]	 43	52 [41]; 76-77	1700, 1600, 1520	5.88 (1 H, s, CH=C), 7.00, 7.44, and 7.58 (each 1 H, dd, d, and d, J = 3 and 4 Hz, J = 4 Hz, and J = 3 Hz, respectively, thienyl), 15.91 (1 H, s, OH)
 44	T	−78	8	 45	30; 60-63	2730, 1730, 1690	1.25 (6 H, s, CH_3), 9.55 (1 H, s, CHO)
 46	T	0	5	 49	54; oil	1670, 1620, 970	2.15 (3 H, s, CH_3), 5.78 and 6.54 (each 1 H, AB q, J = 17 Hz, (CH=CH)
 47	Z	rt	24	 50	44; oil	2210, 1670	2.21 (3 H, s, CH_3)
 48	T	0	3	 51	60; 53-56	1690, 1610	2.02 (3 H, s, CH_3), 5.45 (1 H, s, CH=C), 15.45 (1 H, s, OH)
48	T	−78	8	 52	32; 281-283	1730, 1695, 1600	5.47 (1 H, s, CH=C), 16.66 (1 H, s, OH)

[a] All microanalyses were within 0.4% of the theoretical values. [b] Reaction conditions are as follows: (1) Catalyst: T, $TiCl_4$; S, $SnCl_4$; Z, $ZnCl_2$. (2) temperature in °C; rt = room temperature. (3) reaction time in hours. [c] ^{13}C NMR ($CDCl_3$) for **23** δ 28.0, 36.6, 38.2, 40.8, 46.6, 117.8, 131.6, 213.2; for **41** δ 28.1, 36.6, 39.1, 41.6, 91.8, 126.9, 128.4, 132.0, 135.7, 185.4, 201.3. [d] Reaction conditions in brackets correspond to the yields in brackets.

were prepared from the corresponding alkali metal reagents and trimethylsilyl chloride, except for **6** and **28** which were purchased from Petrarch Systems Inc. Silyl enol ethers **7**, **38**, **40**, **42**,[21] and **44** were prepared according to House's method.[22] Chloroform and dichloromethane used as reaction solvents were dried over $CaCl_2$, distilled, and kept over 4-Å molecular sieves.

Reaction of 4 with Silver Triflate. A solution of **4** (262 mg, 1 mmol) in dry benzene (4 mL) was added to a suspension of silver triflate (260 mg, 1 mmol) in dry benzene (6 mL) at room temperature, and the mixture was stirred overnight in the dark. The products were extracted with hexane after being poured into water and dried over Na_2SO_4. Evaporation of the solvent left a solid, which was chromatographed with hexane to give 160 mg (40%) of 1-phenyladamantane identical with an authentic sample.[23]

Reaction of 5. To a solution of **5** (194 mg, 1 mmol) and **6** (135 mg, 1.2 mmol) in CH_2Cl_2 (8 mL) was added trimethylsilyl triflate (0.1 mL of 0.5 M CH_2Cl_2 solution), and this solution was stirred for 24 h at room temperature. The reaction mixture was then poured into water, and the products were extracted with hexane followed by washing with aqueous Na_2CO_3 and drying over Na_2SO_4. The residue after evaporation of the solvent was chromatographed with hexane to give 125 mg (71%) of **8** as an oil. Similarly **7** gave **9** in 43% yield. These products were identical with those obtained by our previous method.[3a] Allene **11** was prepared in this way in 46% yield from **10**: IR (neat) 1970 cm^{-1}; ^1H NMR (CCl_4) δ 4.62 and 4.64 (each 1 H, d, J = 8 and 5 Hz, respectively, C=C=CH_2), 4.91 (1 H, dd, J = 8, 5 Hz, HC=C=C. Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.30; H, 10.69.

Reaction of 12. $TiCl_4$ (0.11 mL, 1 mmol) in CH_2Cl_2 (8 mL) was added to a solution of **6** (135 mg, 1.2 mmol) and **12** (224 mg, 1 mmol), obtained from **2** with hexamethyldisilazane and trimethylsilyl chloride (1:1),[24] in CH_2Cl_2 (2 mL) at −78 °C. After 15 min of stirring, the mixture was poured into water, and the products were extracted with hexane. The residual oil after evaporation of the solvent was subjected to trap-to-trap distillation [oven temperature 130 °C (3 mmHg)] to give 120 mg (68%) of **8**. The similar treatment of **12** with **7** followed by chromatography (benzene) gave **9** in 71% yield.

Reaction of 16. A mixture of **15**[25] (168 mg, 1 mmol) and bis(trimethylsilyl)acetamide (0.5 mL) was heated at 85 °C for 5 h (the method applied for **2** was not effective), and the resulting solution was poured onto ice. The product was quickly extracted with hexane and dried over Na_2SO_4. Evaporation of the solvent left an oil (**16**) which was dissolved in CH_2Cl_2 (10 mL) containing **6** (270 mg, 2,4 mmol). To this solution was added $TiCl_4$ (0.22 mL, 2 mmol) in CH_2Cl_2 (1 mL) at −78 °C, and the resultant solution was stirred for 15 min. The same work up as above and chromatography (hexane) gave 110 mg (51%) of **14** as an oil: IR (neat) 1645, 1000, 915 cm^{-1}; ^1H NMR (CCl_4) δ 1.82 (4 H, d, J = 7 Hz, CH_2C=C), 4.7–5.1 (6 H, m, CH=CH_2). Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.66; H, 11.34.

Reaction of 17. A solution of **17** (185 mg, 1 mmol) and **6** (135 mg, 1.2 mmol) in CCl_4 (4 mL) was added to $AlCl_3$ (134 mg, 1 mmol) in CCl_4 (6 mL) at 0 °C, and the mixture was stirred at this temperature for 3 h. The usual workup as above gave an oil which was chromatographed with hexane to give 140 mg (74%) of **18** as an oil: IR (neat) 1620, 1000, 910 cm^{-1}; ^1H NMR (CCl_4) δ 1.91 (2 H, d, J = 7 Hz, CH_2C=C), 4.7–6.1 (3 H, m, CH=CH_2). Anal. Calcd for $C_{14}H_{22}$: C, 88.42; H, 11.58. Found: C, 88.51; H, 11.69. A mixture of chloride (37:67 **17**/**21**) gave the same product and the same yield. Similar treatment of **7** with the chloride mixture at 0 °C for 6 h and then at room temperature for 12 h gave 160 mg (65%) of **19**: mp 80–82 °C; IR (KBr) 1700 cm^{-1}; ^1H NMR (CCl_4) δ 1.1–2.4 (26 H, m, ring H). Anal. Calcd for $C_{17}H_{26}O$: C, 82.93; H, 10.57. Found: C, 82.90; H, 10.60.

Reaction of 22. A solution of **22** (200 mg, 1 mmol) and unsaturated organosilane (1 mmol) in CH_2Cl_2 (2 mL) was added to Lewis acid (1 mmol) in CH_2Cl_2 (3 mL) at the temperature designated in Table I and stirred for an appropriate time. Then the reaction mixture was poured into ice–water containing Na_2CO_3, extracted with CH_2Cl_2 (it is sometimes convenient to separate precipitates by filtration with Celite), and dried over Na_2SO_4. Evaporation of the solvent left the residue, which was chromatographed with $CHCl_3$ or recrystallized from hexane to give a product; see Table I for yield, melting point, and spectral data.

Reactions of Adamantane-Substituted Unsaturated Silanes 46–48. The reagents were prepared according to the reported methods.[18,22]

(1) **46**: A solution of 2-(1-adamantyl)vinyl bromide[26] (600 mg, 1.6 mmol) in dry THF (6 mL) was added to a mixture of trimethylsilyl chloride (435 mg, 4 mmol) and granular magnesium (60 mg) in dry THF (5 mL) at room temperature under a nitrogen atmosphere and stirred for 4 h. The reaction mixture was poured into aqueous $NaHCO_3$, and the products were extracted with ether and dried over Na_2SO_4. Filtration through a short silica gel column (Kieselgel 60) and evaporation of the solvent gave crude **46** (260 mg) which had IR absorptions at 1615, 1250, and 850 cm^{-1} ^1H NMR and (CCl_4) signals at δ 0.03 (9 H, s), 5.33 (1 H, d, J = 18 Hz), and 5.84 (1 H, d, J = 18 Hz).

(2) **47**: (1-Adamantyl)acetylene[26] (320 mg, 2 mmol) in dry ether (10 mL) was treated with *n*-butyllithium (1.5 mL of a 1.6 M hexane solution) at room temperature for 1 h and subsequently with trimethylsilyl chloride (260 mg, 2.4 mmol) at reflux temperature for 6 h. The same workup as above gave **47** (360 mg) which had IR absorptions at 2180, 1250, and 840 cm^{-1} and a ^1H NMR (CCl_4) signal at δ 0.10 (9 H, s).

(3) **48**: A solution of **54** (177 mg, 1 mmol) in dry THF (3 mL) was added to lithium diisopropylamide (prepared from 1.2 mmol of diisopropylamine and 0.75 mL of a 1.6 M *n*-butyllithium in hexane solution) in THF (2 mL), and after being stirred for 30 min, this solution was treated with trimethylsilyl chloride (185 mg, 1.7 mmol) at room temperature for 12 h. The usual workup followed by trap-to-trap distillation [oven temperature 120 °C (2 mmHg)] gave **48** (240 mg) which had IR absorptions at 1640 and 1250 cm^{-1} and ^1H NMR (CCl_4) signals at δ 0.11 (9 H, s) and 3.80 and 3.89 (each 1 H, AB q, J = 2 Hz). The thus-prepared reagents were used for the next step without further purification. The reactions of these silanes with acetyl chloride were performed exactly in the same manner as employed for **22**. The reaction conditions and physical data are also displayed in Table I.

Reaction of 53. A solution of **53** (164 mg, 1 mmol) and the silane **6**, **7**, or **25** (1 mmol) in CH_2Cl_2 (3 mL) was added to a solution of $TiCl_4$ (0.11 mL, 1 mmol) in CH_2Cl_2 (3 mL) at 0 °C and stirred for 8 h. The same workup as for **22** and chromatographic separation ($CHCl_3$) gave the following products.

55: 49%; mp 55–58 °C; IR (KBr) 3390, 1640, 990, 910 cm^{-1}; ^1H NMR (CCl_4) δ 1.34 (1 H, s, OH, disappeared with D_2O), 2.99 (1 H, dd, J = 3, 10 Hz, CHOH), 4.8–6.1 (3 H, m, CH=CH_2). Anal. Calcd for $C_{14}H_{22}O$: C, 81.55; H, 10.68. Found: C, 81.43; H, 10.80.

56: 39%; IR (neat) 3500, 1635, 1600, 1500, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.78 (1 H, d, J = 5 Hz, CHOH), 3.94 (1 H, dd, J = 5, 7.5 Hz, CHPh), 4.7–6.3 (3 H, m, CH=CH_2), 7.16 (5 H, br s, phenyl). Anal. Calcd for $C_{20}H_{26}O$: C, 85.11; H, 9.22. Found: C, 84.86; H, 9.21.

57: 29%; IR (neat) 1690, 1610 cm^{-1}; ^1H NMR (CCl_4) δ 5.14 (1 H, t, J = 2 Hz). Anal. Calcd for $C_{17}H_{24}O$: C, 83.61; H, 9.84. Found: C, 83.41; H, 10.04.

Reaction of 58. A solution of **58**[27] (235 mg, 1 mmol) and **6** (135 mg, 1.2 mmol) in CH_2Cl_2 (4 mL) was added to a solution of $TiCl_4$ (0.11 mL, 1.mmol) in CH_2Cl_2 (6 mL) at −78 °C, and after being stirred at this temperature for 4 h, the reaction mixture was worked up as for **22**. Chromatographic separation ($CHCl_3$) gave 100 mg (42%) of **59**: mp 75–77 °C; IR (KBr) 1620, 1290, 1140, 990, 930 cm^{-1}; ^1H NMR (CCl_4) δ 3.55 (2 H, d, J = 6 Hz, CH_2SO_2), 5.1–6.1 (3 H, m, CH=CH_2). Anal. Calcd for $C_{13}H_{20}O_2S$: C, 65.00; H, 8.33. Found: C, 64.93; H, 8.40.

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Registry No. 2, 768-95-6; 3, 77418-99-6; 4, 768-93-4; 5, 22635-62-7; 6, 762-72-1; 7, 6651-36-1; 8, 22922-62-9; 9, 41031-34-9; 10, 13361-64-3; 11, 74203-26-2; 12, 36960-53-9; 13, 16104-50-0; 14, 22922-66-3; 15, 5001-18-3; 16, 70017-41-3; 17, 770-70-7; 18, 82112-68-3; 19, 82112-69-4; 21, 27011-47-8; 22, 2094-72-6; 23, 82094-36-8; 24, 14579-08-9; 25, 19752-23-9; 26, 82094-37-9; 27, 82094-38-0; 29, 2170-06-1; 30, 1578-33-2; 31, 18245-28-8; 32, 82094-39-1; 33, 82094-40-4; 34, 82094-41-5; 35, 7450-03-5; 36, 1459-55-8; 37, 82094-42-6; 38, 19980-43-9; 39, 82094-43-7; 40, 13735-81-4; 41, 82094-44-8; 42, 62889-07-0; 43, 82094-45-9; 44, 6651-34-9; 45, 82094-46-0; 46, 82094-47-1; 47, 82094-48-2; 48, 82094-49-3; 49, 82094-50-6; 50, 82094-51-7; 51, 82094-52-8; 52, 82094-53-9; 53, 2094-74-8; 54, 1660-04-4; 55, 82094-54-0; 56, 82094-55-1; 57, 82094-56-2; 58, 24053-96-1; 59, 82094-57-3; 60, 82094-58-4; 61, 64741-22-6; 62, 24886-73-5; silver triflate, 2923-28-6; 1-phenyl adamantane, 780-68-7; trimethylsilyl triflate, 27607-77-8; bis(trimethylsilyl)acetamide, 10416-58-7; 2-(1-adamantyl)vinyl bromide, 57040-44-5; trimethyl silyl chloride, 75-77-4; acetyl chloride, 75-36-5.

Thiol Acidities and Thiolate Ion Reactivities toward Butyl Chloride in Dimethyl Sulfoxide Solution. The Question of Curvature in Brønsted Plots

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Acidities of 15 benzenethiols and 5 aliphatic thiols have been measured in dimethyl sulfoxide solution. Homohydrogen bonding of the type $PhS^-\cdots HSPh$, which is strong for phenols in Me_2SO, is absent from thiophenols. On the other hand, evidence for strong intramolecular hydrogen bonding was found for the $2\text{-}HOC_6H_4S^-$ anion. A Brønsted plot for the rates of reaction of nine ArS^- ions with BuCl in Me_2SO vs. pK_a for ArSH was found to give an excellent correlation extending over 9 pK units ($\beta = 0.409 \pm 0.003$; $R^2 = 0.9998$). This is contrasted with a Hammett plot for ArSH acidities, which gave a poorer correlation ($R^2 = 0.988$) despite the selection of the five "best" points. A Brønsted plot for log k vs. pK_a for five RS^- ions reacting with BuCl gave a poor correlation over a 5-pK-unit range with a much smaller slope ($\beta = 0.19 \pm 0.03$; $R^2 = 0.91$). The strict linearity of Brønsted plots in Me_2SO solution when basicities are changed by remote substitution is contrasted with the apparent curvature of some Brønsted plots in hydroxylic solvents. It is concluded that the curvature in the latter instances may be an artifact caused by the necessity of using several different families of bases in order to construct the extended Brønsted plots and by the failure to control proximity effects. Attempts to displace a thianion or carbanion by S_N2 attack of a strongly basic anion on the benzyl carbon atom of $PhCH_2SPh$ or 9-$PhCH_2$-9-PhFl were unsuccessful. It is concluded that the intrinsic barriers for these reactions ($\Delta G_0^{\ddagger}$) must be high (>25 kcal/mol) and that homolytic bond dissociation energies are of little use in predicting their size. The general conclusion is drawn that for many reactions there is relatively little variation in transition-state structure for an appreciable change in the thermodynamics of the overall reaction and that theoretical postulates such as the generalized Hammond postulate, the reactivity–selectivity principle, or the variable transition-state theory can have little or no applicability for such reactions.

The question of curvature in Brønsted plots for proton transfers and other types of reactions[1] has evoked considerable discussion in recent years.[4-8] The question is of fundamental import since linearity means that β in the rate-equilibrium relation (eq 1) remains constant, whereas

$$\delta(\Delta G^{\ddagger}) = \beta\delta(\Delta G^{\circ}) \qquad (1)$$

curvature indicates that β in eq 1 is variable. The assumption that the size of β in eq 1 varies with changes in ΔG°, approaching zero for highly exoenergetic reactions and approaching unity for highly endoenergetic reactions, is the basis for a number of widely used theoretical postulates, including the generalized Hammond postulate,[9]

(1) The Brønsted equation, e.g., $\log k_B = \beta \log K_{BH} + C$, is a general relationship that can be applied to all kinds of reactions between donors and acceptors. For example, the equation can be used for reactions of a series of bases (donors) not only with an acid but also with an alkyl halide,[2] an electron acceptor,[3] or any other kind of electrophile.

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(9) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338. In its restrictive form the Hammond postulate refers to transition states and intermediates of nearly the same energy and does not require β to change. However, Hammond suggested that the value of the postulate derives from its application to highly endothermic reactions where the products will provide the best models for the transition states or to highly exothermic reactions where the reactants will provide the best models. It is this generalized form, which requires β to change, that is most commonly invoked. Evidence for an increase in β in a series of deprotonations as ΔG° was made more positive had been observed some years earlier by Bell and Lidwell.[10]

(10) The changes in β observed by Bell and Lidwell for the deprotonation of a series of β-diketone, β-keto ester, and ketone substrates by RCO_2^- bases[11] was the principal experimental evidence cited by Leffler and Grunwald for the assumption that β in eq 1 would vary between the limits of 0 and 1.[12] They recognized the generality of Brønsted-type relationships and believed that changes in β would also be general. This idea was formulated into the reactivity–selectivity principle (RSP). In a recent extensive review of the reactivity–selectivity principle, Pross concludes that "despite many apparent failures the RSP is fundamentally valid".[13]

(11) Bell, R. P.; Lidwell, O. M. *Proc. R. Soc. London, Ser. A* **1940**, *176*, 88–113.

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