Other Assignments. With signal multiplicity data obtained from off-renance experiments, the assignments for carbons 9, 10, 11, and OCH_3 were straightforward and consistent with ^{13}C chemical shifts reported for similar carbon groups.

Experimental Section

Nmr Spectra. ^{13}C nmr spectra were determined at 24.92 MHz on a modified JEOL JNM-PS-100 Fourier-transform spectrometer interfaced with a Nicolet 1085 Fourier-transform computer system. Spectra were obtained in either chloroform-*d* ($CDCl_3$) or dimethyl sulfoxide-d_6 (DMSO-d_6) in 10-mm tubes. The spectra were recorded at ambient temperature by using the deuterium resonance of $CDCl_3$ or DMSO-d_6 as the internal lock signal. All proton lines were decoupled by a broad-band (~2500 Hz) irradiation from an incoherent 99.075-MHz source. Interferograms were stored in 8*K* of computer memory (4*K* output data points in the transformed phase corrected real spectrum), and chemical shifts were measured on 5000-Hz sweep width spectra. Typical pulse widths were 12 μsec, and the delay time between pulses was fixed at 1.0 sec. Normally 512 (twice as many for single frequency off-resonance experiments) data accumulations were obtained on a 200 mg/2 ml of solvent sample. The chemical shifts reported are believed accurate to within ±0.05 ppm.

Chemicals. Cinchonidine and quinine were obtained from Sigma Chemical Co. Quinidine was purchased from Aldrich Chemical Co. 9-Epiquinine and 9-epiquininidine were prepared by conversion of the natural alkaloid tosylate.[17] The dihydro alkaloids were prepared by reduction of the corresponding unsaturated alkaloid in ethanol using 10% palladium on carbon catalyst. The melting points and $[\alpha]_D$ values of all the compounds synthesized were in agreement with literature values.

Acknowledgment. We thank Dr. M. E. Wall of this laboratory for his kind encouragement and support of this work and Dr. S. G. Levine, North Carolina State University at Raleigh, for helpful discussions involving this work.

Registry No.—I, 485-71-2; II, 130-95-0; III, 572-60-1; IV, 56-54-2; V, 572-59-8; VI, 522-66-7; VII, 1435-55-8; VIII, 51743-68-1.

References and Notes

(1) This investigation was supported by Contract PH-43-NIGMS-65-1075 from the National Institute of General Medical Sciences, National Institutes of Health.

(2) (a) North Carolina State University at Raleigh; (b) Research Triangle Institute.

(3) (a) R. B. Turner and R. B. Woodward in "The Alkaloids," Vol. 3, R. Manske, Ed., Academic Press, New York, N. Y., 1953, pp 1–63; (b) M. R. Uskakovic and G. Grethe, *ibid.*, Vol. XIV, 1973, pp 181–223.

(4) W. O. Crain, Jr., W. C. Wildman, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93,** 990 (1971).

(5) E. Wenkert, J. S. Bindra, C.-J. Chang, D. W. Cochran, and F. M. Schell, *Accounts Chem. Res.*, **7,** 46 (1974).

(6) L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43,** 1245 (1971).

(7) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86,** 2984 (1964).

(8) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972, Chapter 3, and references cited therein.

(9) D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, **89,** 5315 (1967).

(10) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **94,** 5318 (1972).

(11) Reference 8, p 54.

(12) Dreiding stereomodels.

(13) The ^{13}C nmr spectra of cinchonidine in $CDCl_3$ and in DMSO-d_6 contain three singlets and six doublets for the nine carbons of the quinoline ring.

(14) Reference 8, p 81.

(15) For quinoline in $CDCl_3$ the ^{13}C chemical shifts of C-9′ and C-10′ are at 128.0 and 148.0 ppm, respectively, and for 4-methylquinoline in $CDCl_3$ C-9′, C-4′, and C-10′ are at 127.9, 143.9, and 147.7 ppm, respectively.

(16) Reference 8, p 100.

(17) J. Suszko and F. Szelog, *Bull. Int. Acad. Pol. Sci. Lett., Cl. Sci. Math. Natur., Ser. A,* 403 (1935).

Reductive Defunctionalization of 1-Substituted Adamantanes in Molten Sodium Tetrachloroaluminate

V. R. Koch, L. L. Miller,*[1] and R. A. Osteryoung

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521

Received January 25, 1974

The reactivity of a number of substituted adamantanes in molten $NaAlCl_4$ at 175° was assessed. Those substituents with Lewis base character reacted with the melt to give adamantane and chloroadamantane. Neutral and Lewis acid substituents were recovered unchanged. Cyclic voltammetry revealed adamantane and 1-methyladamantane to be electroactive at a tungsten electrode well within the background limits of molten $NaAlCl_4$.

The use of molten salt media to effect a variety of organic transformations both homogeneously and at an electrode has recently been reviewed.[2] No reference was made, however, to the kinds of reactions undergone by aliphatic compounds in these ionic, aprotic solvents. Accordingly, we set out to survey the chemical stability of 1-substituted adamantanes (1-Ad-X) in a nominally 50:50 mol % $AlCl_3$–NaCl melt at 175°. By examining the behavior of a representative number of functionalities in this medium an appreciation of their reactivity or inertness can be achieved.

The availability of monofunctionalized bridgehead adamantanes and their resistance to skeletal rearrangement make them an ideal model system with which to probe the reactivity of different substituents. Indeed, the anodic behavior of a series of 1-Ad-X in acetonitrile has been reported.[3] Of particular interest to us is the feasibility of doing organic electrosynthesis in molten salts. Cyclic voltammetry indicates that electrochemically generated oxidation intermediates of aromatic amines,[4] sulfur heterocycles,[5] and polycyclic aromatic hydrocarbons[6] are stabilized by the melt.

While the exact nature of this phenomenon is unknown, it appears that the absence of a nucleophilic organic solvent and the associated trace amounts of water accounts for the greatly extended lifetime of these reactive intermediates. If simple aliphatic cation radicals or cations are similarly stabilized it should be possible to do preparative electrochemistry without the chemical follow-up reactions common to organic solvent–electrolyte media.

Results and Discussion

The results of adding 1-Ad-X to approximately 5 ml of melt are summarized in Tables I–III. Substituents with Lewis base character reacted with the melt to give mixtures of adamantane, chloroadamantanes, hydrogen chloride, and, in two instances, carbon monoxide. Neutral and electrophilic substituents either complexed with the

Table I
Adamantyl Compounds Defunctionalized by 50:50 Mol % $AlCl_3$–NaCl Melt

Registry no.	X	1-Ad-X, mmol	% conversion	
			Ad-H	1-Ad-Cl[a]
768-92-3	F	0.36	25	0.2
935-56-8	Cl	0.80	28	0.2
768-90-1	Br	1.23	28	0.2
6221-74-5	OMe	0.63	38	9.5
768-95-6	OH	0.84	41	8.0
768-94-5	NH_2[b]	1.12	16	1.3
	NH_2[c]	1.18	13	1.7
828-51-3	CO_2H[d]	0.57	23	0.4
711-01-3	CO_2Me[d]	0.97	21	0.4

[a] Trace amounts of 2-Ad-Cl detected. [b] 0.30 mmol of 1-Ad-NH_2 recovered. [c] Reaction time doubled; 0.29 mmol of 1-Ad-NH_2 recovered. [d] Carbon monoxide evolved.

Table II
Effect of Melt Composition on Product Distribution

Melt composition, mol % $AlCl_3$	X	1-Ad-X		% conversion		Isolated residue, mg
		Mmol	Mg	Ad-H	1-Ad-Cl	
49.75	Br	1.89	403	30	0.7	90
	CO_2H	0.91	164	18	0.5	60
50.00	Br	1.23	264	28	0.2	50
	CO_2H	0.57	103	23	0.4	25
64.00	Br	1.47	316	Trace		132
	CO_2H	1.13	203	Trace		102

melt or sublimed out of solution. In these cases, 1-Ad-X was recovered unchanged.

1-Haloadamantanes. When added to the clear, colorless sodium tetrachloroaluminate at 175°, 1-fluoro-, 1-chloro-, and 1-bromoadamantane formed an immediate deep red solution with concomitant evolution of a white sublimate. This material was quantitatively collected and weighed. Though the reaction was over in 3–5 min the solution was maintained at 175° for 15 min prior to cooling and work-up of the solidified melt.

Infrared spectra of each of the gas mixtures sampled from above the melts showed the rotational fine structure and ν_0 characteristic of hydrogen chloride. Neither HBr nor HF were detected. Nmr spectra of the three sublimates revealed the presence of adamantane and 1-chloroadamantane. Further analysis of the sublimate disclosed a third product in trace amounts which had the same retention time as authentic 2-chloroadamantane. No starting material was found in the 1-bromo- and 1-fluoroadamantane sublimates.

The melt was pulverized and continuously extracted with ether. This led to the isolation of a gold, resinous material which could not be fully characterized. This substance was recovered from the solidified melt whenever 1-Ad-X reacted with sodium tetrachloroaluminate.

It is instructive to compare the products from the reaction of 1-chloroadamantane and aluminum chloride in carbon tetrachloride at room temperature to the products from the reaction of 1-chloroadamantane and melt reported in Table I. Kovacic and Chang[7] found that after 1 hr 10% adamantane, 75% 1-chloroadamantane, 2% 2-chloroadamantane, and 13% dichloroadamantane were obtained in contrast to the 30% yield of adamantane formed in the melt. Conceivably, the high temperature of the molten salt in conjunction with its Lewis acid properties effect a more rapid and complete dehalogenation.

To guarantee that loss of substituent was in fact due to the melt and not temperature alone, 1-bromoadamantane, which possesses the weakest 1-adamantyl carbon–substituent bond, was heated to 190° and maintained at that temperature for 5 min. After cooling, 1-bromoadamantane was recovered unchanged. Thus, there is no reason to suspect that the other substituents were cleaved by thermal decomposition.

An important feature of sodium tetrachloroaluminate melts is the ability to precisely vary the Lewis acidity over nine orders of magnitude. Boxall and coworkers[8] have completely described the equilibria of the various species comprising a melt over a range of 50–70 mol % aluminum chloride. In the region immediately about 50 mol % aluminum chloride, the predominant species are given by the equilibrium

$$2AlCl_4^- \overset{K_m}{\rightleftharpoons} Al_2Cl_7^- + Cl^-$$

where $Al_2Cl_7^-$ is considered to be a Lewis acid, and Cl^-, a Lewis base; $K_m = 1.06 \times 10^{-7}$ at 175°. The addition of small amounts of either aluminum chloride or sodium chloride to the melt dramatically shifts the above equilibrium as per Figure 1.

Table III
Adamantyl Compounds Stable to 50:50 Mol % $AlCl_3$–NaCl Melt

Registry no.	X	1-Ad-X, mol	% recovery
281-23-2	H	0.77	98[a]
768-91-2	Me	0.57	88[a]
23074-42-2	CN	0.72	88
1660-04-4	COMe	0.72	89
700-58-3	2 =O	0.82	90

[a] Sublimed out of melt; others recovered by continuous extraction of pulverized melt with ether.

To determine the effect of melt composition and thereby the Lewis acidity on product distribution, 1-bromoadamantane was added to melts with aluminum chloride adjusted to 49.75 (Cl^- saturated) and 64.00 mol %. These

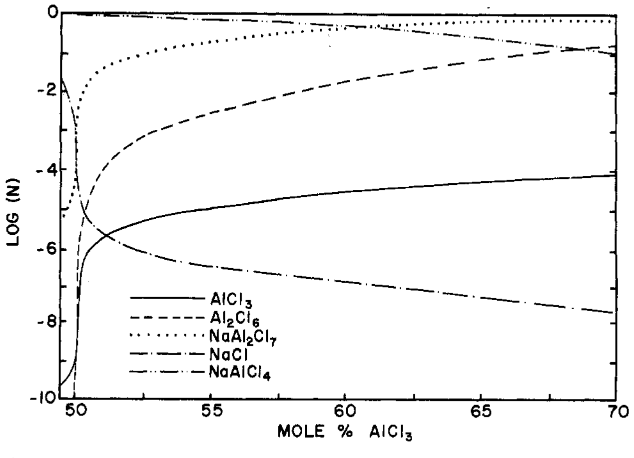


Figure 1. Mole fraction of the species in the chloroaluminate melt at 175° as a function of the net $AlCl_3$-NaCl ratio (49.75 ≤ mol % $AlCl_3$ ≤ 70).

values correspond to chloride ion (Lewis base) concentrations of 8.85×10^{-2} and 4.13×10^{-7} M, respectively. For comparison, the chloride ion concentration in 50 mol % aluminum chloride is 2.87×10^{-2} M.

As seen in Table II, very little change in either overall yield or product distribution occurs in going from 49.75 to 50.00 mol % aluminum chloride. At 64.00 mol % aluminum chloride, however, only trace amounts of adamantane were recovered while the quantity of organic residue extracted from the melt increased. Clearly, abrupt changes in the Lewis acidity are reflected in the product distribution.

The nature of the nonsublimable product is of interest not only because it is the major product of the reaction, but also because the amount formed is dependent upon melt composition. Accordingly, an attempt was made to delimit at least the gross structural features of this material.

The nmr spectra and glc traces of all isolated resins were virtually identical regardless of adamantyl functionality or melt composition. The complexity of this material is exemplified by glc analysis, which revealed five major and 15 minor components eluting closely together. When chromatographed on a silica gel column two distinct fractions were obtained, the first eluting with Skellysolve and the second with chloroform.

Fraction 1, a yellow oil comprising 59% of the resin by weight, included five major and ten minor closely eluting components by glc. The nmr spectrum of this fraction was virtually identical with that of the resin itself and exhibited a broad downfield absorption at δ 5.4 and absorptions from δ 3 to 0.8 characteristic of aliphatic protons. Infrared analysis disclosed a broad carbonyl band at 1705 cm^{-1}. An average molecular weight of 427 amu was calculated from vapor pressure osmometry measurements. This value agrees with mass spectrometric data in that the "parent" ion cluster was observed to occur between m/e 425 and 430. The base peak was m/e 135, indicative of the adamantyl cation.

Fraction 2 eluted as a dark red oil and accounted for the remainder of the resin. One major and six minor closely eluting components were indicated by glc. The nmr spectrum contained a distinct though broad doublet at δ 4. Aliphatic absorptions between δ 3 and 0.6 made up the rest of the spectrum. The infrared spectrum revealed a broad band from 3600 to 3200 cm^{-1} due to O–H stretch. A carbonyl band similar in shape to that in fraction 1 at 1720 cm^{-1} was also evident. Vapor pressure osmometry measurements gave an average molecular weight of 752 amu.

From the spectroscopic data it appears that fraction 1 contains ketone and the adamantyl moieties. In addition, fraction 2 includes hydroxyl functionalities. It is noteworthy that the proton geminal to the hydroxy group in 2-adamantanol absorbs at δ 3.8 in the nmr spectrum.[9] This value is close to the δ 4.0 resonance observed in the spectrum of fraction 2. Neither 1- nor 2- adamantanol was found in fraction 2.

Since all reductive defunctionalizations were conducted in a scrupulously dry nitrogen atmosphere, oxygen incorporation can only ensue during the work-up of the organics extracted from the melt and most probably from water, not oxygen. This was supported by infrared analysis of a chloroform extract prior to work-up. Neither hydroxy nor carbonyl bands were observed in the spectrum. In an attempt to scavenge nascent cations a chloroform extract was treated with anhydrous methanol, distilled to dryness, and the nmr spectrum taken. With the exception of a singlet at δ 3.5 indicative of a methyl ether functionality the spectrum was identical with that of the usual resin.

Oxygen-Substituted Adamantanes. Like the haloadamantanes, 1-adamantanol and 1-methoxyadamantane formed instantaneous dark red solutions when added to the melt with hydrogen chloride evolution. The sublimates of these compounds contained the best overall conversion to adamantane and chloroadamantane.

A similar reductive defunctionalization of 1-adamantanol with other Lewis acids has recently been reported. In either n-hexane or carbon disulfide 1-adamantanol reacted with aluminum bromide to give adamantane and 1-bromoadamantane; with tin tetrachloride 1-chloroadamantane was obtained.[10]

1-Aminoadamantane. This compound was partially stable in the melt as evidenced by the recovery of some unreacted amine *via* continuous extraction. Relatively small amounts of adamantane and 1-chloroadamantane were found. To ascertain if the amine was reacting slowly in comparison to the other substituents, this experiment was repeated, the reaction time being doubled. As seen in Table I there was no increase in sublimate yield and the amount of recovered amine remained constant.

1-Adamantyl Carboxylate Derivatives. When either 1-adamantanecarboxylic acid or 1-carbomethoxyadamantane was added to the melt a dark red solution was formed with copious gas evolution. Infrared spectra of the reaction gases confirmed the presence of carbon monoxide as well as hydrogen chloride.

The formation of carbon monoxide and *tert*-butyl cation from pivalyl chloride under Friedel–Crafts conditions is well documented.[11–13] Olah and coworkers[14] have found that pivalyl fluoride and antimony pentafluoride react to give carbon monoxide and *tert*-butyl cation. This facile decarbonylation was ascribed to the Lewis acid character of the antimony pentafluoride.

Mechanistic Aspects of Reductive Defunctionalization. By analogy with earlier work under Friedel–Crafts conditions[15] it is clear that C–X cleavage begins with the coordination of nonbonding substituent electrons with an electron-deficient species in the melt. The heptachlorodialuminate ion, $Al_2Cl_7^-$, free aluminum chloride, and its dimer, Al_2Cl_6, have all been shown to exist simultaneously in the melt[8] and are likely candidates. From the melt composition diagram (Figure 1) it is evident that above 55 mol % aluminum chloride concentrations of the more acidic $AlCl_3$ and Al_2Cl_6 species increase relative to the concentration of the $Al_2Cl_7^-$ ion. This is reflected in the sensitivity of 1-bromoadamantane and 1-adamantanecarboxylic acid reactions to precipitous changes in melt composition.

In any case, generation of 1-adamantyl cations leads directly to the volatile products: adamantane by hydride abstraction, and 1-chloroadamantane by reaction with a chloride-containing species in the melt.

This rationale is consistent with work done on 1-haloadamantanes in other Lewis acid systems. Schleyer and coworkers[16] identified 1-adamantyl cations as products of the reaction of 1-fluoro- or 1-chloroadamantane with antimony pentafluoride. When generated in the presence of pentane, 1-adamantyl cations were found to abstract hydride ion to give adamantane.[17] On the other hand, adamantane itself was found to be inert to strong Lewis acids. In molten aluminum bromide, for example, this hydrocarbon was recovered unchanged.[18] Since the sodium tetrachloroaluminate melt is free of organic material, the source of hydride ion must be substrate itself. This most certainly accounts for the partitioning of products between the sublimables (adamantane and monochloroada-

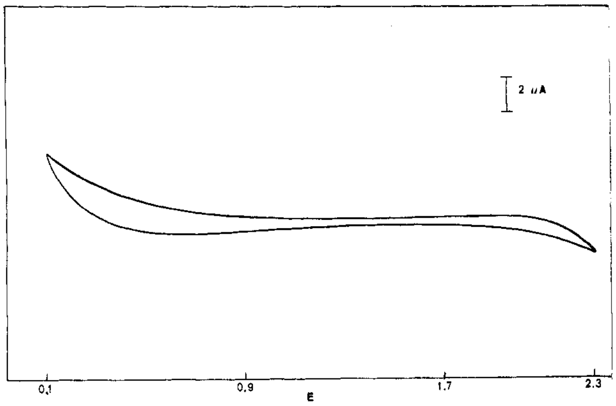


Figure 2. Cyclic voltammogram of melt background; sweep rate 200 mV/sec.

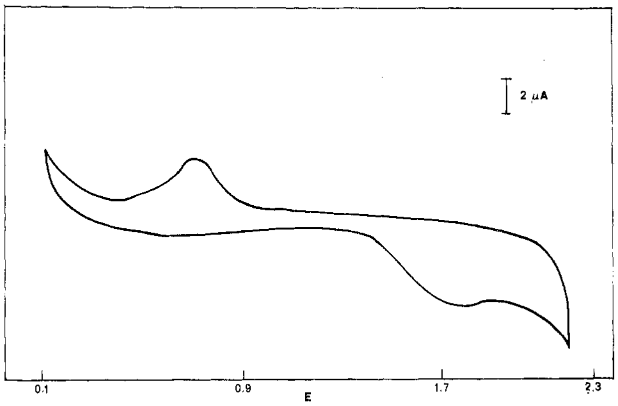


Figure 3. Cyclic voltammogram of adamantane or 1-methyladamantane at 200 mV/sec.

mantane) and the nonvolatile resinous material recovered from the melt.

The source of proton for hydrogen chloride is unclear. That proton does not exist in the melt prior to addition of substrate has been demonstrated by cyclic voltammetry, to be discussed later. Hydrogen chloride was identified as a reaction product in the chlorination of adamantane by ferric chloride and antimony pentachloride.[7] However, a free-radical mechanism was invoked to account for its formation. The chlorination of alcohols and acylation of carboxylic acids by aluminum chloride provides hydrogen chloride as a by-product.[19] However, in the absence of acidic substrate protons no hydrogen chloride is produced.

Adamantane and 1-Methyladamantane. These aliphatic hydrocarbons were stable to as well as soluble in the melt, though at 175° sublimation was rapid (Table III).

Cyclic voltammograms (Figures 2–4) were performed at a tungsten electrode at various sweep rates. At 200 mV/sec both compounds manifested an anodic wave, E_p = 1.80 V *vs.* an aluminum wire reference. The peak potential was sweep rate dependent and no reversible cathodic waves were observed at scans up to 100 V/sec. A cathodic wave, E_p = 0.70, absent in the voltammogram of background, was evident whenever the first and subsequent sweeps passed through the anodic wave. This process was determined to be the reduction of proton to hydrogen.

Cyclic voltammograms of melts through which hydrogen chloride had been bubbled show an identical cathodic wave, E_p = 0.70.

Adamantyl Ketones and Cyanide. All three of these compounds (Table III) formed stable complexes with the medium. When 1-acetyladamantane or 2-adamantone was added to the melt a light tan solution ensued. No sublimation was noted. Cyclic voltammograms of these solutions were identical with the voltammogram of background. Upon cooling and continuous extraction with ether good yields of starting material were recovered. When 1-cyanoadamantane was added to the melt a bright yellow solution resulted. Again, no sublimate was collected and a good yield of starting material was obtained.

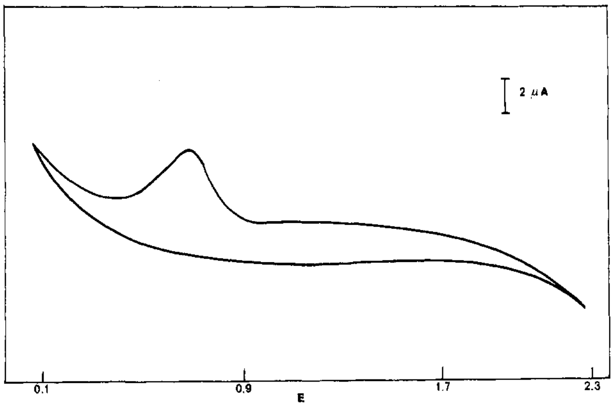


Figure 4. Cyclic voltammogram of melt through which anhydrous HCl has been bubbled; sweep rate 200 mV/sec.

It has been reported that aromatic nitriles and ketones are stable in an aluminum chloride melt, the latter forming a 1:1 complex with $AlCl_3$.[2] Olah and Calin[20] working in SbF_5-FSO_3H-SO_2 at −60° find that a variety of alicyclic ketones, including 2-adamantone, are stable albeit protonated in this Lewis acid medium.

Experimental Section

General. Starting materials and products were analyzed by ir on a Perkin-Elmer 457 grating spectrometer. Nmr spectra were taken on a Varian T-60 instrument. Glc analyses were performed on a Hewlett-Packard Model 5700 gas chromatograph equipped with thermal conductivity detectors. A 10 ft × 0.25 in., 8% SE-30 on Chromosorb W column was used for all determinations of product distribution. Average molecular weights were determined in chloroform at 30° with a Hewlett-Packard 302B vapor pressure osmometer. Mass spectra were recorded with an A.E.I. Model MS-12 spectrometer.

Dried Fluka A.G. (anhydrous, iron free) aluminum chloride and Fisher reagent-grade sodium chloride were quantitatively weight out into a Pyrex cell under a purified nitrogen atomosphere (Vacuum/Atmospheres Corp. drybox equipped with a HE-493 Dri-Train). The details of the cell and the electrolysis purification procedure are described elsewhere.[21] The purified melt (*ca.* 50:50 mol %) was completely clear and colorless. A Thermo Electric Model 400 thermoelectric controller was used to maintain the temperature of the melt at 175 ± 0.5°. The temperature was measured using a Chromel-Alumel Pyrex-sheathed thermocouple and a Fluke 8000A digital multimeter.

Materials. Adamantane, 2-adamantone, 1-bromoadamantane, 1-adamantanol, 1-aminoadamantane, 1-acetyladamantane, and 1-adamantanecarboxylic acid were commercial samples (Aldrich) and were used without further purification. 1-Carbomethoxyadamantane was supplied by Professor G. J. Gleicher. The other 1-substituted adamantanes were prepared as described previously.[3] 2-Chloroadamantane was obtained by the reduction of 2-adamantone to 2-adamantanol with lithium aluminum hydride followed by chlorination with phosphorus pentachloride.[7]

Reactions of 1-Ad-X with the Melt. All reactions were carried out in the drybox. In a typical run, 5 ml of molten salt was pipetted from the cell into a 30 × 80 mm Pyrex test tube preheated to and maintained at 175° *via* an aluminum block furnace. The test tube was fitted with a 29/26 female joint. A preweighed amount of 1-Ad-X was added to the melt and the test tube was immediately mated with a sublimation tower vented at the top. The sublimation tower was made by first sealing the end of a 30 × 150 mm Pyrex tube fitted with a 29/26 male joint and then opening up a small hole in the seal to which a short piece of 8-mm Pyrex tubing was attached. The length of the tower was heated and a number of Vigreux-type indentations were made. This simple device afforded a convenient and efficient method of quantitatively collecting material which sublimed out of the melt.

After 15 min at 175° with occasional swirling the sublimation tower was separated from the test tube, brought out of the dry-box, allowed to cool, and weighed. The contents were rinsed off the indentations with chloroform and subjected to glc as well as spectral analysis. The melt was allowed to cool, then pulverized and continuously extracted for 24 hr with ether. After 3 × 100 ml water washes the organic layer was dried over magnesium sulfate and concentrated on a Roto-Vap. Whenever 1-Ad-X reacted with the melt a tarry gold substance resulted which proved to be a complex mixture of substituted aliphatic hydrocarbons.

Gaseous products were detected by attaching an evacuated 10-cm Perkin-Elmer demountable gas cell to the sublimation tower *via* a short length of Tygon tubing. The observed ν_0 values for hydrogen chloride and carbon monoxide agreed with published data.[22]

Cyclic Voltammetry. Cyclic voltammograms were recorded with a PAR Model 170 electrochemistry system. The reference electrode was an aluminum wire (Alfa, m5N) separated from the working and counter electrodes by a fine glass frit. The melt in the reference compartment was saturated with sodium chloride. The working electrode, isolated in its own fritted compartment, was a 30-mil tungsten wire (Alfa, m3N8) sealed into a Pyrex tube with a bead of uranium glass, ground flat on an emery wheel and polished with 600 grit silicon carbide powder. The counter electrode was an aluminum wire.

Cyclic voltammograms were run at approximately 10^{-3} *M* substrate concentrations at 50, 100, 200, and 500 mV/sec. E_p values are quoted for rates of 200 mV/sec.

Acknowledgment. This work was supported by the U. S. Army Research Office (Durham) under Grant DA-ARO-D-31-124-73-G18.

References and Notes

(1) Fellow of the Alfred P. Sloan Foundation.
(2) H. L. Jones and R. A. Osteryoung, *Advan. Molten Salt Chem.*, in press.
(3) V. R. Koch and L. L. Miller, *J. Amer. Chem. Soc.*, **95**, 8631 (1973).
(4) H. L. Jones, L. G. Boxall, and R. A. Osteryoung, *J. Electroanal. Chem.*, **38**, 476 (1972).
(5) K. W. Fung, J. Q. Chambers, and G. Mamantov, *J. Electroanal. Chem.*, **39**, 81 (1973).
(6) M. Fleischmann and D. Pletcher, *J. Electroanal. Chem.*, **25**, 449 (1970).
(7) P. Kovacic and J. Chang, *J. Org. Chem.*, **36**, 3138 (1971).
(8) L. G. Boxall, H. L. Jones, and R. A. Osteryoung, *J. Electrochem. Soc.*, **120**, 223 (1973).
(9) R. C. Fort, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).
(10) E. A. Shokova, S. I. Knopova, and B. A. Kazanskii, *Dokl. Akad. Nauk SSSR*, **212**, 386 (1973); *Chem. Abstr.*, **79**, 136610n (1973).
(11) E. Rothstein, *et al.*, *J. Chem. Soc.*, 581 (1958).
(12) A. Balaban and C. Nenitzescu, *Justus Liebigs Ann. Chem.*, **625**, 66 (1959).
(13) H. Hogeveen and C. F. Roobeck, *Recl. Trav. Chim. Pays-Bas*, **89**, 1121 (1970).
(14) G. Olah, *et al.*, *J. Amer. Chem. Soc.*, **85**, 1328 (1963).
(15) G. Olah and M. Meyer, "Friedel-Crafts and Related Reactions," Vol. I, G. Olah, Ed., Interscience, New York, N. Y., 1965, Chapter VIII.
(16) P. v. R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow, and G. Olah, *J. Amer. Chem. Soc.*, **86**, 4195 (1964).
(17) G. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **90**, 933 (1968).
(18) P. v. R. Schleyer and M. M. Donaldson, *J. Amer. Chem. Soc.*, **82**, 4645 (1960).
(19) G. Olah, "Friedel-Crafts and Related Reactions," Vol. I, G. Olah, Ed., Interscience, New York, N. Y., 1965, Chapter II.
(20) G. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 938 (1968).
(21) L. G. Boxall, H. L. Jones, and R. A. Osteryoung, *J. Electrochem. Soc.*, **121**, 212 (1974).
(22) K. Nakamoto, "Infra-red Spectra on Inorganic and Coordination Compounds," Wiley-Interscience, New York, N. Y., 1970.

Silalactones from Hydrosilyl Derivatives of Toluic Acids

Joanne M. Wolcott and Frank K. Cartledge*

Louisiana State University at Baton Rouge, Baton Rouge, Louisiana 70803

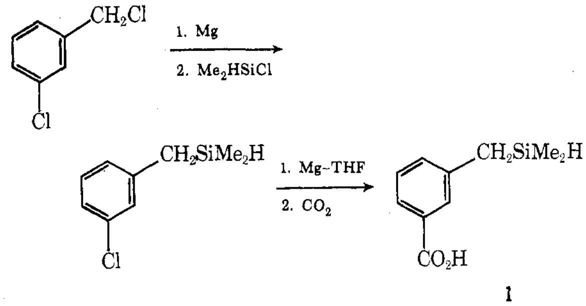
Received March 12, 1974

The preparation of 3- and 4-carboxybenzyldimethylsilane is reported, along with conversion of the acids under pyrolytic and hydrolytic conditions to dimeric or polymeric silalactones and to silanols and disiloxanes. In some cases, rather complex equilibria involving the various products can be displaced to result in virtually exclusive formation of one product. Of particular interest is a novel macrocyclic lactone dimer in the meta series which can be obtained in good yield. A general method for the preparation of silalactones is proposed, and the monomeric lactone from 2-carboxybenzyldimethylsilane is reported. Spectral properties of the products are reported and discussed.

The possible interactions between an aromatic ring and a Si atom β to the ring have been the subject of intense investigation in recent years. Two types of interactions have been proposed, first, a 1,3 p–d bonding in which electron density is donated from the phenyl ring to an empty d orbital on Si,[1] and second, a hyperconjugative interaction involving a C–Si σ bond.[2] Either type of interaction could give rise to hindered rotation about the ring to benzyl carbon bond. This restriction to rotation of the side chain could in principle be observed by variable-temperature nmr, since the methylene protons or the methyl groups on silicon would become diastereotopic and potentially distinguishable when an ortho or meta substituent is present. To investigate this possibility, 3-carboxybenzyldimethylsilane (**1**) was prepared. The carboxy group was chosen because of its anticipated ease of synthesis and because of the relatively large effects of carbonyl groups on chemical shifts of nearby protons. We chose to study the meta derivative first so that we could be sure that we would not be observing a steric interaction between the carboxyl and silylmethyl groups.

Results and Discussion

All attempts to prepare **1** by using standard Grignard preparations (eq 1) were unsuccessful. Although there is



(1)

1

ample precedent for the generation of a C–Mg bond in the presence of a Si–H bond,[3] it is usually necessary to use forcing conditions to generate Grignards from aryl chlorides. Indeed, the only method that resulted in the formation of the Grignard reagent from *m*-chlorobenzyldimethylsilane involved the use of powdered Mg,[4] prior activation