

Initial Products in Friedel-Crafts Reactions

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SnCl_4 and AlCl_3 form ternary complexes with ketones and HCl in sulfur dioxide solvent. These complexes are the initial products in aromatic Friedel-Crafts acylations. Heats of formation from ketone- AlCl_3 adduct and HCl were calculated from the temperature dependence of the equilibrium constants. Relative reactivities are presented for acylation with AlCl_3 and SnCl_4 at low temperature in sulfur dioxide solution.

Introduction

Complexes of oxygen-containing compounds with AlCl_3 and SnCl_4 are well-known. More specifically with compounds of interest in Friedel-Crafts reactions the systems AlCl_3 -acetyl chloride and AlCl_3 -acetophenone have been studied in sulfur dioxide solution.^{2,3} Complexes of a convenient model compound, dimethyl ether, with AlCl_3 ⁴ and SnCl_4 have been carefully studied.⁵⁻⁷ Hydrogen chloride, a possible product in the Friedel-Crafts reaction, has been reported to form complexes with dimethyl ether.⁸ A complex of two molecules of acetophenone with SnCl_4 has also been described.⁹ There does not appear to be any mention of ternary complexes of an oxygen-containing organic compound, hydrogen chloride, and AlCl_3 or SnCl_4 . It seemed desirable to investigate spectroscopically all these species under comparable conditions in order to identify the initially formed products in the acylation of a simple aromatic compound by acetyl chloride, where ketone, hydrogen chloride, and metal chloride are all nominally present in the reaction mixture.

The relative reactivities of AlCl_3 and SnCl_4 in the acylation of toluene have been reported.¹⁰ However, this was evaluated from the yield of final product after workup of the mixture and may be different than the relative rate constants for formation of an initial complex product. Therefore an attempt has been made to determine the relative reactivities with AlCl_3 and SnCl_4 from the proton resonance spectra of the reaction mixture itself after reaction had proceeded to only a slight extent.

Experimental Section

Chemicals. Aluminum chloride was purified by repeated vacuum sublimation, sealed in glass ampules under vacuum, and used shortly thereafter. The contents of freshly opened containers of germanium tetrachloride and tin tetrachloride were transferred in a drybox under dried nitrogen to containers closed by Teflon high-vacuum stopcocks. All nitrogen was then removed by freeze-pump-thaw cycles. Silicon tetrachloride was fractionally distilled under argon with a Vigreux column. The argon was then removed by freeze-pump-thaw cycles. Hydrogen chloride was used directly from the supplier's cylinder. Dimethyl ether was dried over LiAlH_4 and then transferred into a container with a Teflon high-vacuum stopcock on the vacuum line. Acetyl

chloride, benzene, toluene, mesitylene, *p*-xylene, acetophenone, sulfur dioxide, and neopentane were purified and used as previously described.¹¹ Methyl mesityl ketone was prepared from mesitylene, acetyl chloride, and aluminum chloride in carbon tetrachloride. Hydrochloric acid was added to the initial product complex. The liquid was washed with dilute sodium hydroxide solution and water. It was then dried with anhydrous calcium chloride and the solvent was flash distilled. The free ketone was obtained by vacuum distillation of this final product with a Vigreux column and its identity confirmed by proton resonance spectroscopy. It was stored under nitrogen over 4 Å molecular sieves.

Sample Preparation. Samples were prepared by condensing the appropriate quantities of sulfur dioxide, neopentane, dimethyl ether/acetyl chloride, tin/germanium/silicon tetrachloride, and hydrogen chloride (with/without), all measured as vapors, into an NMR tube equipped with a Teflon high-vacuum stopcock and then sealed under vacuum. The contents were thawed, mixed, and stored at -80°C . Samples containing benzene, toluene, and *p*-xylene were prepared starting as above, then the contents were thawed and mixed, and the walls of the tubes were washed by distillation of solvent from the solution of the lower part. Finally a known quantity of aromatic hydrocarbon, also measured as vapor, was condensed into the sample tube, which was then sealed under vacuum. The tube was quickly thawed, mixed, and stored at -80°C . Samples containing either AlCl_3 (solid) or relatively nonvolatile liquids such as mesitylene, acetophenone, and methyl mesityl ketone were prepared by at first transferring them into NMR tubes closed with Teflon high-vacuum stopcocks in a drybox. After these substances were weighed, the appropriate quantities of sulfur dioxide, neopentane, and other reagents, measured as vapors, were condensed into the NMR tube, and the procedure continued as mentioned above. Those samples containing both AlCl_3 and ketones were prepared by using an NMR tube closed with a Teflon high-vacuum stopcock that had a sidearm separated from the main tube by a second Teflon high-vacuum stopcock. The AlCl_3 was transferred into the side arm in a drybox and the amount was weighed. The ketone was then transferred into the main tube and the amount was also obtained by weighing. Sulfur dioxide, neopentane, and (or without) hydrogen chloride, measured as vapors, were transferred into the sidearm containing AlCl_3 . The contents of the sidearm were thawed, mixed, and then delivered into the main tube, which contained the ketone. The walls of the tube were washed by distillation of solvent from the solution in the lower part of the main tube. Finally the main tube was sealed under vacuum, thawed, mixed, and stored at -80°C . In the case of samples containing mesitylene, acetyl chloride, and tin tetrachloride, in order to avoid rapid reaction upon thawing at room temperature, the condensed mixture was only partially thawed to melt those parts in contact with the walls of the tube. Complete thawing and mixing were quickly done in a methanol-dry ice bath. It was immediately equilibrated at -64°C in the NMR probe and the spectrum taken.

Magnetic Resonance Measurements. Proton, ^{13}C , and ^{119}Sn resonance spectra were obtained on a Varian Associates XL100 spectrometer equipped with Nicolet Fourier Transform and multinuclear attachments. All spectra are reported with respect

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Table I. Chemical Shifts and Equilibrium Constants for Dimethyl Ether-HCl Complex Formation

$T, ^\circ\text{C}$	δ complex	K	pairings
-74	3.86 ± 0.09	880 ± 560	5
-64	3.84 ± 0.05	240 ± 110	3
-44	3.71 ± 0.05	110 ± 30	4
-4	3.72 ± 0.05	12 ± 2	2

Table II. Concentrations of Dimethyl Ether-SnCl₄ Solutions in SO₂^a

sample	SnCl ₄	(CH ₃) ₂ O
C	0.004 79	0.003 74
D	0.004 76	0.009 50
E	0.004 76	0.010 2
F	0.004 71	0.029 5

^a Concentrations are given in mole fractions.

to tetramethylsilane although neopentane was used as internal reference. Corrections applied were 0.92 ppm for protons and 31.4 ppm for ¹³C. ¹¹⁹Sn resonances were also referenced to neopentane by a direct frequency comparison with its ¹³C resonances and then corrected to Sn(CH₃)₄ as zero. Temperature calibration and peak area measurements were done as previously reported.^{3,11}

Results and Discussion

Since the complexation of dimethyl ether by hydrogen chloride was studied by relatively crude techniques,⁸ a simple reinvestigation at several temperatures was undertaken by proton resonance spectroscopy in sulfur dioxide as solvent. A single averaged line for free and complexed dimethyl ether and another for free and complexed HCl are found at all temperatures. Since there are two unknowns, the equilibrium constant for complex formation and the chemical shift of the complexed species, two samples of different and known initial composition are required to solve for the two unknowns. Since an analytic solution is very complex, a simple computer program was written that iterated by varying the chemical shift assumed for the complex until equal values were obtained for the equilibrium constant of the two samples. Documentation of the program is contained in the supplementary material. Four samples of different, known, composition were prepared and their chemical shifts measured at four different temperatures. It is possible to make six different pairings among four samples. The calculated results and average deviations are listed in Table I. The results are very

sensitive to the observed chemical shift, especially at higher temperature. Under these circumstances only pairings of samples with rather different concentrations can be employed. The number of pairings is also listed in Table I. From the temperature dependence of the equilibrium constant the heat of formation of the complex is calculated to be 6.2 ± 0.4 kcal/mol. It was not feasible to add sufficient excess of HCl to drive the equilibrium entirely to the complex form without generating a dangerously high sample pressure should the sample be warmed to room temperature.

The system AlCl₃-(CH₃)₂O has been studied in sulfur dioxide.⁴ The system SnCl₄-(CH₃)₂O has been studied by proton resonance spectroscopy in methylene chloride.⁶ Both cis and trans isomers were observed with equal proton-tin coupling constants. In order to allow exact comparisons among all the data work on the SnCl₄-(CH₃)₂O system was repeated in sulfur dioxide as solvent. The chemical shift, spin coupling, cis-trans ratio, and relative rates of exchange for the cis and trans complexes with free ligand agree with those previously reported. However exchange between the cis complex and free ligand is immeasurably fast in sulfur dioxide solution. Even in the case where excess SnCl₄ is present and there is no measurable concentration of uncomplexed dimethyl ether, there is a rapid exchange of ligands between molecules of the cis complex, shown by complete averaging of the ¹H-Sn coupling constants. This is strong evidence that exchange between two molecules of the cis complex occurs by a bimolecular reaction. Since such a reaction is so facile, it is probable that exchange between the cis complex and free dimethyl ether occurs by an associative mechanism in sulfur dioxide solution. A dissociative mechanism is postulated in methylene chloride solution.⁶ Rate data were obtained for four samples whose composition is listed in Table II. The lifetimes and rate data are presented in Table III. From these the energy and entropy of activation are calculated to be 13.9 ± 0.6 kcal/mol and -15 eu for the sample with an excess of SnCl₄ and 15.2 ± 0.8 kcal/mol and -8 eu for the average of the other three samples. If exchange between cis and trans complexes occurs by partial dissociation of the complex, the activation energy for exchange must be equal to or greater than the heat of formation of the complex from the acidic and basic species. The heats of formation for these complexes have not been reported but by analogy with AlCl₃ complexes,

Table III. Equilibria and Rate Data for Exchange between Trans and Cis Complexes of Dimethyl Ether-SnCl₄

$T, ^\circ\text{C}$	sample	[trans]/[cis]	$\tau_{\text{trans}}, \text{s}$	$\tau_{\text{trans}}/[\text{trans}]$	$k_{\text{exch}}, \text{s}^{-1}$
-34	C	0.56	0.84	625	0.001 60
	D	0.68	1.03	268	0.003 73
	E	0.51	0.76	221	0.004 52
	F	0.25	1.25	212	0.004 72
-24	C	0.56	0.20	149	0.006 71
	D	0.61	0.18	50	0.020 0
	E	0.49	0.35	103	0.009 71
	F	0.25	0.38	64	0.015 6
-14	C	0.49	0.064	52	0.019
	D	0.61	0.055	15	0.067
	E	0.51	0.061	18	0.056
	F	0.25	0.075	13	0.077
-4	C	0.47	0.024	20	0.050
	D	0.61	0.018	5.0	0.20
	E	0.49	0.021	6.2	0.16
	F	0.25	0.028	4.7	0.21
+6	C	0.49	0.011	9.1	0.109
	D	0.49	0.009 9	3.2	0.31
	E	0.53	0.011	3.1	0.32
	F	0.25	0.012	2.0	0.50

Table IV. Proton Chemical Shifts of Some Complex Species

compd	δ CH ₃	compd	δ CH ₃	compd	δ COCH ₃
(CH ₃) ₂ O	3.20	C ₆ H ₅ COCH ₃	2.64	MMK	2.49
(CH ₃) ₂ O·HCl	3.83	C ₆ H ₅ COCH ₃ ·HCl	3.26	MMK·HCl	2.74
(CH ₃) ₂ O·AlCl ₃	4.16	C ₆ H ₅ COCH ₃ ·AlCl ₃	3.32	MMK·AlCl ₃	3.39
2[(CH ₃) ₂ O]·AlCl ₃	3.88	2(C ₆ H ₅ COCH ₃)·AlCl ₃	3.25	2(MMK)·AlCl ₃	3.21
2[(CH ₃) ₂ O]·SnCl ₄ trans	4.03	2(C ₆ H ₅ COCH ₃)·SnCl ₄ trans	3.14		
2[(CH ₃) ₂ O]·SnCl ₄ cis	3.88	2(C ₆ H ₅ COCH ₃)·SnCl ₄ cis	3.23	2(MMK)·SnCl ₄	3.14
(CH ₃) ₂ O·AlCl ₃ ·HCl	4.53	C ₆ H ₅ COCH ₃ ·AlCl ₃ ·HCl	3.50	MMK·AlCl ₃ ·HCl	3.25
2[(CH ₃) ₂ O]·SnCl ₄ ·HCl	4.02	2(C ₆ H ₅ COCH ₃)·SnCl ₄ ·HCl	3.54	2(MMK)·SnCl ₄ ·HCl	3.35

Table V. Temperature Dependence for the Formation of the 1:1:1 Complex from (CH₃)₂O·AlCl₃ and HCl

T, °C	% 1:1:1 complex	K _{eq}
-70	22.3	42
-60	15.6	25
-50	13.4	20
-40	8.0	11

which have heats of formation from 10 to 15 kcal/mol,¹² they will be about the value observed for the exchange activation energies. Therefore no firm conclusions can be drawn about the exchange mechanism. The slower exchange rate for the sample with excess SnCl₄, compared with the other samples, is significant and suggests a minor change in mechanism.

Complex formation was not observed between dimethyl ether and SiCl₄ or GeCl₄.

A 1:1:1 complex is formed between AlCl₃, dimethyl ether, and HCl. The chemical shift of the methyl protons, which is directly observable, is listed in Table IV along with those of the other complexes discussed. Formation of the ternary complex occurs to only a slight extent. The structure is presumed to have a five-coordinate aluminum surrounded by four chlorine atoms and the ether oxygen. This oxygen is protonated by the hydrogen arising from the HCl. Support for assignment of such a structure comes from the observation of spin coupling between the acidic proton and the six hydrogens of the coordinated dimethyl ether in an analogous complex with TiCl₄.¹³ For a sample prepared with 0.00884 mole fraction of each reactant the relative concentration of the 1:1:1 complex and the equilibrium constant as a function of temperature are tabulated in Table V. From the temperature dependence of the equilibrium constant the heat of formation of the 1:1:1 complex from (CH₃)₂O·AlCl₃ and HCl is calculated as 4.0 ± 0.4 kcal/mol. At these temperatures exchange between the 1:1 and the 1:1:1 complexes is slow on the NMR time scale.

Evidence for a 2:1:1 complex of dimethyl ether, SnCl₄, and HCl is indirect but nevertheless persuasive. The solid complex of dimethyl ether in contact with a saturated solution is brought completely into solution upon addition of the stoichiometric quantity of HCl gas. Only a single line for the methyl groups is seen in the proton resonance spectrum at all temperatures, with no indication of cis-trans isomerism or tin-proton spin coupling. This suggests rapid exchange between the species making up the complex. The limiting shift with an excess of HCl is listed in Table IV; however both this value and the formula given for the complex cannot be considered certain since separate signals at the slow exchange limit were not observed.

After establishing the existence of ternary compounds of HCl and AlCl₃ or SnCl₄ with the relatively simple Lewis base dimethyl ether, ketones as products of the Friedel-

Table VI. Chemical Shifts and Equilibrium Constants for Acetophenone-HCl Complex Formation

T, °C	δ complex	K	pairings
-84	3.31 ± 0.02	1600 ± 500	3
-74	3.26 ± 0.01	1000 ± 200	3
-64	3.28 ± 0.09	350 ± 180	5
-44	3.21 ± 0.12	80 ± 40	4
-4	2.82	16	1

Table VII. Equilibrium Constants for Formation of the Acetophenone-AlCl₃·HCl Complex and Rates for Its Exchange with the Acetophenone-AlCl₃ Complex

T, °C	[1:1:1]/[1:1]	K _{eq}	k _{exch} , s ⁻¹
-74	1.31	377	
-64	0.71	152	9.7
-54	0.40	70	19

Table VIII. Chemical Shift of the Acetyl Methyl Group as a Function of Sample Composition

[SnCl ₄]	[acetophenone]	[HCl]	δ CH ₃
2.5	1	2.5	3.536
1	1	1	3.465
1	2.1	1.2	3.379
1	3	1	3.228
1	2.3	2.3	3.407

Table IX. Chemical Shift of the Acetyl Protons of MMK as a Function of Sample Composition

[MMK]	[AlCl ₃]	[HCl]	[SnCl ₄]	δ COCH ₃
2.07	1	0		3.20
1	1.45	0		3.21
1	1	1		3.25
2.17	0	0	1	3.13
1.38	0	0	1	3.14
3.18	0	0	1	2.94
1	0	0	1.5	3.12
1	2	2		3.39
2.3	1	1		3.13
2.9	1	1		3.05

Crafts reaction were investigated. Similar results were obtained with HCl and acetophenone as Lewis base to those with dimethyl ether. They are listed in Table VI. From the temperature dependence of the equilibrium constant the heat of formation of the complex between acetophenone and HCl is calculated to be 6.1 ± 0.3 kcal/mol, the same as that found with dimethyl ether.

Complexes of acetophenone and AlCl₃ have already been described.³ Acetophenone forms a 2:1 complex with SnCl₄. The stoichiometry was established from the constancy of the chemical shift with increasing concentration of acetophenone until a 2:1 ratio with SnCl₄ was reached. With higher acetophenone concentrations the observed shift was the weighted average for the 2:1 complex and free acetophenone. There is rapid exchange with excess free acetophenone and no evidence of cis-trans isomerism. Acetophenone forms a 1:1:1 complex with AlCl₃ and HCl. The stoichiometry of this complex was established by varying the relative concentrations of the reactants. With equal

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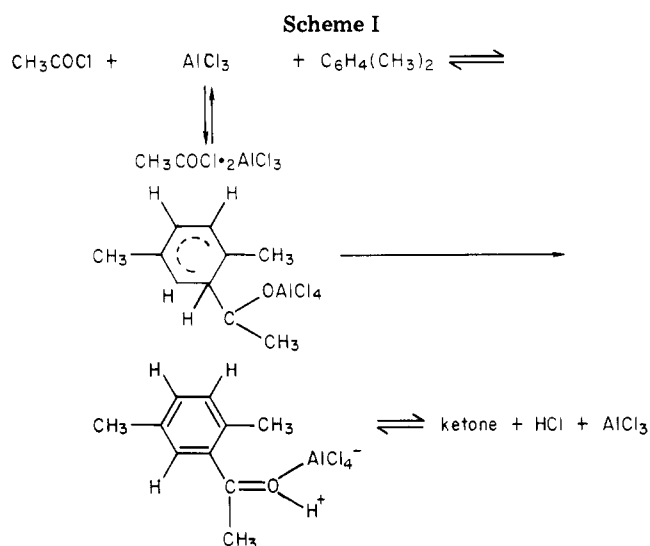
Table X. Concentration Dependence of the Extent of Product Formation

sample	[SnCl ₄]	[CH ₃ COCl]	[mesitylene]	[product]	[product]/ ([SnCl ₄][CH ₃ COCl][mesitylene])
I	0.0116	0.0115	0.0215	0.001 32	460
J	0.0120	0.0119	0.0115	0.000 83	505
K	0.0113	0.0320	0.0113	0.001 98	485
L	0.0113	0.0119	0.0313	0.001 41	335
M	0.0238	0.0116	0.0111	0.001 63	532

concentrations of acetophenone, HCl, and AlCl₃ there are two approximately equal signals from the ternary complex and the 1:1 AlCl₃-acetophenone complex. As the concentration of HCl is increased, the signal from the ternary complex increases and that of the 1:1 complex decreases. When the concentration of acetophenone is increased beyond the 1:1 ratio a single line is observed with chemical shift between that of the 1:1 and 1:2 AlCl₃-acetophenone complexes. Exchange between the methyl proton signals of the 1:1 AlCl₃-acetophenone complex and the 1:1:1 complex is slow at -74 °C but increases such that only a single averaged line is observed at -44 °C. Chemical shifts of the various complex species are listed in Table IV. Relative abundances, equilibrium constants, and approximate exchange rates are tabulated in Table VII for a sample containing 0.00687 mole fraction AlCl₃, 0.00786 mole fraction acetophenone, and 0.00793 mole fraction HCl. From the temperature dependence of the equilibrium constant the heat of formation of the 1:1:1 complex from HCl and the 1:1 complex is found to be 7.2 ± 0.5 kcal/mol. A complex is formed between acetophenone, SnCl₄, and HCl. There is rapid exchange between the various acetophenone species, but the stoichiometry of the ternary complex was established as acetophenone:SnCl₄:HCl 2:1:1 from the change in chemical shift with changes in sample composition. These are listed in Table VIII, and the chemical shift of this complex is also listed in Table IV.

Methyl mesityl ketone (MMK) forms complexes in the same manner as acetophenone. Proton chemical shifts of the acetyl group of MMK and its complexes are listed in Table IV. The stoichiometries of the complexes were determined by changes in chemical shifts with changes in sample compositions. The same procedure was used with MMK and HCl as with dimethyl ether or acetophenone and HCl. In the case of MMK it was possible to iterate upon the chemical shift of both the acetyl and aromatic protons. They both gave similar results for the equilibrium constant. At -84 °C the equilibrium constant was found to be 360 ± 200 and 75 ± 14 at -74 °C. Chemical shifts from which stoichiometries were determined are listed in Table IX.

An attempt was made to determine further details of the structure of the ternary SnCl₄ complex via a multiplicity-determining carbon resonance spectrum.¹⁴ The carbonyl carbon of the ternary complex was not protonated, or bonded to tin, since no carbon-tin satellite signals were observed and it was not strongly spin coupled to any protons. Therefore the complex contains seven-coordinate tin with five chlorine atoms and two oxygens about the central atom. Although seven-coordinate tin species are not common, they are well recognized.¹⁵ The ¹¹⁹Sn resonance of the ternary complex with MMK is found at -366 ppm, which is 65 ppm to higher field than the shift of -301 ppm found for (MMK)₂SnCl₄. This difference agrees with those found for other systems on going from six-coordinate



to seven-coordinate tin.¹³ The existence of seven-, and even eight-, coordinate tin allows low energy pathways for exchange of ligands via displacement reactions.¹⁶ Therefore the rapid exchange of free and complexed ligands in the tin complexes discussed in this article, but not for the aluminum complexes, is readily understandable.

With the establishment of the identity and chemical shifts of all the product species one can interpret the spectra of reaction mixtures in Friedel-Craft reactions. The reaction of acetyl chloride and aluminum chloride with some simple aromatic hydrocarbons has been reported.¹¹ With *p*-xylene as aromatic hydrocarbon an additional product proton resonance signal was reported. It can now be stated by comparison of the present results with those previously reported¹¹ that the species present after a very slight extent of reaction are 2(ketone)·AlCl₃ and free HCl. As the reaction proceeds the concentration of the ternary complex ketone-AlCl₃-HCl grows and gives the additional signal, which was reported. Thus the reaction can be represented by Scheme I.

The second part of this study is the examination of the reaction of SnCl₄ and acetyl chloride with some aromatic hydrocarbons under similar conditions to those used in the reactions with AlCl₃. In contrast to AlCl₃ there is no observable complex formation between SnCl₄ and acetyl chloride. There is no measurable reaction between SnCl₄, acetyl chloride, and benzene, toluene, and *p*-xylene at temperatures as high as room temperature in sulfur dioxide solution. Reaction with mesitylene occurs to some extent immediately upon thawing the sulfur dioxide solutions but thereafter is quite slow at -64 °C. The uncertainty of a zero time for the beginning of the reaction under such circumstances does not allow one to acquire classical kinetic data. As an alternative, when the samples were thawed in a standard manner at low temperature the extent of product formation upon thawing was found to be directly proportional to the product of the concentrations

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of the initially added SnCl_4 , acetyl chloride, and mesitylene. Results, listed in Table X, for five samples whose concentration of SnCl_4 varies by a factor of 2, acetyl chloride by a factor of 3, and mesitylene by a factor of 3, only show an average deviation of 10% in the ratio. Therefore it can be concluded that the extent of reaction is proportional to the concentration of each of the reactants to the first power. This does not necessarily imply a ternary collision since an intermediate, e.g., SnCl_4 -mesitylene, might be formed in very low concentration. As an example of the data used the proton resonance spectrum of sample J just after thawing is on file as supplementary data. From a comparison of the chemical shift of the product with the species listed in Table IV one may conclude that the product is $(\text{MMK})_2\text{SnCl}_4\cdot\text{HCl}$. Since the reaction rate depends upon the concentration of mesitylene to the first power, a very rapid disproportionation of the initially formed product must occur.

A quantitative comparison of the reactivity with SnCl_4 as metal chloride, vis-à-vis AlCl_3 , is not possible since the overall lower reactivity of SnCl_4 did not allow a study with the same substrate at the same temperature. Although SnCl_4 is less reactive, a significant fact is the different order of reactivity of the various aromatic hydrocarbons. Thus

with AlCl_3 toluene is slightly more reactive than mesitylene,¹¹ while with SnCl_4 mesitylene is much more reactive than toluene. Therefore it is not possible to make general statements about relative reactivities. Presumably both the extent of intermediate complex formation and its rate of rearrangement to product affect the overall reactivity.

Registry No. $(\text{CH}_3)_2\text{O}$, 115-10-6; $(\text{CH}_3)_2\text{O}\cdot\text{HCl}$, 24521-77-5; $(\text{CH}_3)_2\text{O}\cdot\text{AlCl}_3$, 14740-73-9; $2[(\text{CH}_3)_2\text{O}]\cdot\text{AlCl}_3$, 34537-62-7; $2[(\text{CH}_3)_2\text{O}]\cdot\text{trans-SnCl}_4$, 63038-95-9; $2[(\text{CH}_3)_2\text{O}]\cdot\text{cis-SnCl}_4$, 55905-92-5; $(\text{CH}_3)_2\text{O}\cdot\text{AlCl}_3\cdot\text{HCl}$, 86822-16-4; $2[(\text{CH}_3)_2\text{O}]\cdot\text{SnCl}_4\cdot\text{HCl}$, 86822-17-5; $\text{C}_6\text{H}_5\text{COCH}_3$, 98-86-2; $\text{C}_6\text{H}_5\text{COCH}_3\cdot\text{HCl}$, 86822-18-6; $\text{C}_6\text{H}_5\text{COCH}_3\cdot\text{AlCl}_3$, 23444-00-0; $2(\text{C}_6\text{H}_5\text{COCH}_3)\cdot\text{AlCl}_3$, 86851-94-7; $2(\text{C}_6\text{H}_5\text{COCH}_3)\cdot\text{trans-SnCl}_4$, 75963-09-6; $2(\text{C}_6\text{H}_5\text{COCH}_3)\cdot\text{cis-SnCl}_4$, 86851-95-8; $\text{C}_6\text{H}_5\text{COCH}_3\cdot\text{AlCl}_3\cdot\text{HCl}$, 86822-19-7; $2(\text{C}_6\text{H}_5\text{COCH}_3)\cdot\text{SnCl}_4\cdot\text{HCl}$, 86822-20-0; MMK, 1667-01-2; MMK-HCl, 86822-21-1; MMK-AlCl₃, 86822-22-2; $2(\text{MMK})\cdot\text{AlCl}_3$, 86822-23-3; $2(\text{MMK})\cdot\text{SnCl}_4$, 86822-24-4; MMK-AlCl₃-HCl, 86822-25-5; $2(\text{MMK})\cdot\text{SnCl}_4\cdot\text{HCl}$, 86822-26-6; CH_3COCl , 75-36-5; $\text{CH}_3\text{COCl}\cdot\text{AlCl}_3$, 26273-09-6; $2(\text{CH}_3\text{COCl})\cdot\text{AlCl}_3$, 86822-27-7; $2,5\text{-}(\text{CH}_3)_2\text{C}_6\text{H}_3\text{COCH}_3\cdot\text{AlCl}_3\cdot\text{HCl}$, 86822-28-8; SiCl_4 , 10026-04-7; GeCl_4 , 10038-98-9; SnCl_4 , 16804-87-8; AlCl_3 , 7446-70-0; *p*-xylene, 106-42-3; benzene, 71-43-2; toluene, 108-88-3; mesitylene, 108-67-8.

Supplementary Material Available: Computer program and NMR data (4 pages). Ordering information is given on any current masthead page.

Synthesis Applications of Cationic Aza-Cope Rearrangements.¹ Stereoselective Synthesis of *cis*- and *trans*-3a-Aryl-4-oxodecahydrocyclohepta[*b*]pyrroles

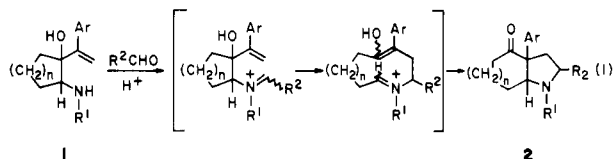
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Received April 11, 1983

A general synthesis of 3a-aryl-4-oxodecahydrocyclohepta[*b*]pyrroles is detailed (eq 1, $n = 2$). The key step is a "ring-enlarging pyrrolidine annulation" reaction which occurs when 2-amino-1-(1-arylvinyl)cyclohexanols are treated at 25–80 °C with an aldehyde and acid. Three different methods (Schemes I and II) for assembling the 2-amino-1-(1-arylvinyl)cyclohexanol intermediates are reported. *cis*-3a-Aryl-4-oxodecahydrocyclohepta[*b*]pyrroles can be formed with complete stereocontrol from either *cis*- or *trans*-2-amino-1-(1-arylvinyl)cyclohexanols. The corresponding *trans* bicyclics can be prepared with modest (~3:1) selectivity from *cis*-2-((diphenylmethyl)amino)-1-(1-arylvinyl)cyclohexanols. The stereochemical outcome of these tandem cationic aza-Cope-Mannich cyclization reactions is consistent with chair topographies for the rearrangement steps (Scheme III).

A useful ring-enlarging pyrrolidine annulation sequence has been recently reported^{1,2} from these laboratories (eq 1). In this reaction, cationic aza-Cope rearrangement

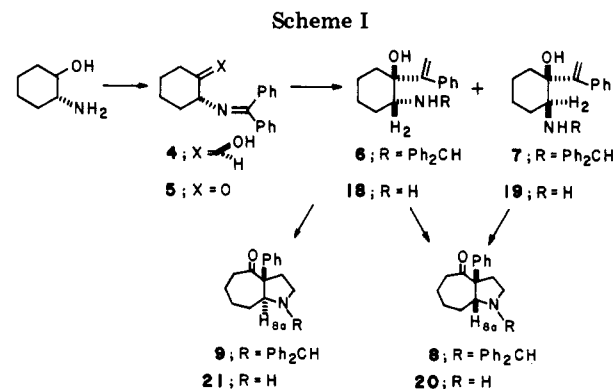


(2-azonia[3,3]sigmatropic rearrangement)³ of iminium ions

(1) Part 13 in the series. For part 12 see: Overman, L. E.; Mendelson, L. T.; Jacobsen, E. J. *J. Am. Chem. Soc.*, in press.

(2) (a) Overman, L. E.; Mendelson, L. T. *J. Am. Chem. Soc.* 1981, 103, 5579. (b) Overman, L. E.; Mendelson, L. T.; Flippin, L. A. *Tetrahedron Lett.* 1982, 23, 2733. (c) Overman, L. E.; Jacobsen, E. J. *Ibid.* 1982, 23, 2741.

(3) For a recent review see: Heimgartner, H.; Hansen, H.-J.; Schmid, H. In "Iminium Salts in Organic Chemistry", Part 2; Böhme, H.; Viehe, J. G., Eds.; Wiley: New York, 1979; pp 655-732.



derived from cyclopentanols ($n = 1$), followed by capture of the azacycloalkadiene isomers in an intramolecular Mannich fashion gave 3a-aryl-4-oxooctahydroindoles ($n = 1$) in good yields.^{1,4} We now wish to describe the details