72 h failed, and the starting material was recovered; although the same treatment of **3** yielded **10** in a yield of 70%.

Measurements of Decomposition of 2 in Aqueous Solution. (1) In Acid Solution. A solution of **2** in dilute H_2SO_4 (0.685×10^{-4} mol/L, pH 1.25) was kept at 25 °C for 24 h. Absorption coefficients at 210 (ϵ 10730) and 241 nm (10790) indicated that decomposition of 30–40% of **2** had occurred. These values imply that the half life $\tau_{1/2}$ of **2** is 32–47 h.

(2) In Neutral Solution. Since the rate of the decomposition of **2** in a buffer solution of pH 7.39 (Michaelis phosphate) was too rapid to follow, the increase in intensity at 241 nm arising from the generation of **1** was measured instead. To the stirred buffer solution (100 mL) was added a solution (2.00 mL) of **2** in acetonitrile (2.00 mL, 3.50 mmol/L) at 25 °C, and from the resulting solution, several aliquots (each 5.00 mL) were removed at 30-s intervals and quenched with 2 N HCl (0.10 mL). The extinction coefficient of every aliquot was almost the same, indicating that the decomposition was completed in less than 30 s.

(3) Isolation of Alkaline Hydrolysis Products of 2. To a stirred solution of sodium hydroxide (1.0 mol/L, 30 mL), immersed in an ice–water bath, was added portionwise **2** (2.76 g, 12 mmol), and then the resulting solution (pH above 11.0) was stirred for 1.5 h after removal of the bath. The solution was acidified with 2 N HCl to pH 1.5. The acid solution was treated with an excess of ethereal solution of diazomethane, and the resulting mixture was extracted with ethyl acetate. The organic layer was washed with water and dried (Na_2SO_4), and then the solvent was removed. The residue was chromatographed on silica gel, and elution with benzene–ethyl acetate (2:1) afforded a 3:1 mixture of **4** and **5** in a yield of 96.8% calculated by the equation shown in Scheme II. Repeated chromatography gave pure samples of **4** and **5**, which were identified respectively with authentic samples of **4** and **5** prepared by similar treatments of pure **1**. **4**: UV λ_{max}^{EtOH} (ϵ) 223.0 nm (3700); ^{1}H NMR ($CDCl_3$) δ 2.80 (s, 3 H, SMe), 3.95 (s, 3 H, NMe); ^{13}C NMR ($CDCl_3$) δ 15.3 (SMe), 33.3 (NMe), 155.0 (ring carbon). **5**: UV λ_{max}^{EtOH} (ϵ) 246.0 nm (14500); ^{1}H NMR ($CDCl_3$) δ 3.90 (s, NMe); ^{13}C NMR ($CDCl_3$) δ 34.9 (NMe), 164.7 (ring carbon).

The aqueous layer was freeze-dried under high vacuum, giving a colorless powder, which was dissolved in methanol. Removal of the inorganic salts by filtration and concentration of the methanol solution in vacuo gave an oil, which was purified by bulb to bulb distillation at 90 °C (10 μmHg). Crystallization of the distillate from ethanol–*n*-hexane gave **7**, mp 34–35 °C (lit.[6] mp 36 °C), in a yield of 50% calculated by the equation in Schemes I and II. **7**: IR $\nu_{max}^{CHCl_3}$ 3160, 1715, 1496 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.18 (s, 3 H, NMe), 8.65 (s, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ 34.66 (NMe), 143.33 (=CH). Anal. Calcd for $C_2H_4N_4$: C, 28.57; H, 4.80; N, 66.64. Found: C, 28.59; H, 4.99; N, 66.26.

Thiol–Disulfide Exchange Reaction between 2 and 1. (1) ^{1}H NMR Spectra of Mixtures of 1 and 2. ^{1}H NMR spectra of mixtures of various ratios of **1** to **2**, dissolved in $CDCl_3$ (10 mg/0.60 mL), were measured at 23 °C under the following conditions for FT NMR measurements: spectral width, 2200 Hz; acquisition time, 5.0 s; pulse width, 4 μs (pulse flipping angle, 27°); number of data points, 22K; number of transients, 4. A single sharp signal of the NMe group was observed for each mixture, and the observed δ values for the mixtures with the molar ratios of **1** to **2**, shown in the parentheses, were as follows: 3.933 (100/0); 3.988 (88.9/11.1); 4.032 (75/25); 4.083 (57.1/42.9); 4.135 (33.3/66.7); 4.182 (0/100).

(2) Measurement of Line Widths of ^{1}H NMR Signals of a Mixture of 1 and 2. The half-height widths of the ^{1}H NMR signals of the mixtures of various ratios of **1** to **2**, dissolved in $CDCl_3$ (1.00 mL), were measured at 23 °C under the following conditions for FT NMR measurements: spectral width, 2000 Hz; acquisition time, 7.998 s; pulse width, 3 μs; number of data points, 32K; number of transients, 4. The observed half-height widths (Hz) for the mixtures, of which weights (mg) of **1** and **2** are shown in parentheses, were as follows: 0.62 (0.0, 10.0); 0.63 (0.5, 10.0); 0.66 (5.0, 10.0); 0.58 (5.0, 0.0). The observed increases in the half-height widths were within the experimental error (0.10 Hz), and the order of the rate of the exchange (k) was estimated to be larger than 10^5 mol^{-1} s^{-1}, which was calculated from the increase in line width ($\lesssim$0.1 Hz) by using the equations for a rapid two-site exchange process given by Smallcombe and Caserio.[10d]

Thiol–Disulfide Exchange Reaction between 2 and 3. (1) Isolation of 10. To a solution of **3** (925 mg) in dichloromethane (25 mL) was added portionwise **2** (1.451 g) under a nitrogen stream, and the resulting mixture was stirred at room temperature for 1.5 h. Colorless crystals precipitated and were collected by filtration and then washed with dichloromethane, giving **10** (358 mg, 39%), mp 131–132 °C. **10**: ^{1}H NMR (Me_4SO-d_6, 90 MHz, Varian EM-90 NMR spectrometer) δ 2.74, 3.03 (AB q, d, J = 13, 10, 1.5 Hz, 4 H, CH_2), 3.40 (m, 2 H, CHO), 5.16 (d, J = 4 Hz, 2 H, OH). Anal. Calcd for $C_4H_8O_2S_2$: C, 31.55; H, 5.31; S, 42.12. Found: C, 31.22; H, 5.07; S, 42.11. The structure was also confirmed by comparison of its IR spectrum and melting point with those reported previously.[11]

(2) UV Measurements of the Rate of the Exchange Reaction in Acetonitrile. Since the rate of the exchange reaction of **2** with **3** even in a diluted acetonitrile solution was too rapid to follow, the increase in the intensity at 241 nm arising from the generation of **1** was measured instead. A solution of **2** in acetonitrile (0.065 mmol/L, 2.00 mL) was shaken in a cell with a solution of **3** in acetonitrile (0.065 mmol/L, 2.00 mL) at 25 °C, and the UV spectra of the resulting solution were measured in a rapid-scan mode with a Hitachi 320 UV spectrometer after 30, 90, 120, and 480 s. The intensity at 241 nm of the first measurement remained constant thereafter, confirming that the reaction had been completed in less than 30 s.

(3) ^{1}H NMR Measurements of Yields of the Exchange Reaction between 2 and 3 in Neutral Aqueous Solution. In order to prepare a D_2O phosphate buffer solution (0.2 mol/L, pD 7.0, μ 0.5) with a lower content of H_2O, a D_2O solution of $Na_2HPO_4 \cdot 12H_2O$ (366.4 mg), $NaH_2PO_4 \cdot 2H_2O$ (152.4 mg), and NaCl (55.8 mg) was freeze-dried, and the residue was dissolved in D_2O (10.0 mL). To a solution of **3** (10 mmol/L) in the D_2O buffer solution were added various amounts of **2** corresponding to the concentrations shown in Table II, and the ^{1}H NMR spectra of the resulting solutions were measured at 37 °C immediately after complete dissolution under the following conditions for FT NMR measurement: spectral width, 1100 Hz; acquisition time, 5.0 s; pulse width, 7 μs; pulse interval 10 s; number of data points, 10K; number of transients, 128. Although the SCH_2 signals for **3** [δ ca. 2.72 (m) and ca. 2.76 (m)] and **10** [δ ca. 2.93 (m) and ca. 3.15 (m)] were well separated and the yield of **10** was calculated on the basis of the ratio of the intensity of the SCH_2 signal for **10** to the summations of both the intensities of the SCH_2 signals for **3** and **10**, it is noteworthy that a long pulse interval (10 s) was necessary to obtain the accurate ratio of the intensities because of the T_1 problem. Since some error in weighing the samples of **2** was inevitable, the molar ratio was determined exactly by the ratio of the integrated intensity of the NMe signal for the generated **1** to the summation of the intensities of the SCH_2 signals for both **3** and **10**.

Registry No. **1**, 13183-79-4; **2**, 62671-38-9; (±)-**3**, 27565-41-9; **4**, 68700-68-5; **5**, 54986-14-0; **7**, 16681-77-9; (±)-**10**, 86023-22-5.

Mechanism of Friedel–Crafts Acetylation of Acetylene with Acetyl Chloride

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The Friedel–Crafts acylation of alkynes, leading to the formation of β-chlorovinyl ketones has long been known.[2] The addition of acid chlorides to acetylene in the presence of aluminum chloride at 0 °C in carbon tetrachloride yields solely *trans*-β-chlorovinyl ketones.[3] Other workers re-

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ported the formation of *E* and *Z* isomers from the reaction of $AlCl_3$, acid chlorides, and several alkynes in dichloromethane.[4] These β-chlorovinyl ketones did not isomerize under the reaction conditions. On the other hand, *cis*-β-chlorovinyl ketones prepared by the reaction of hydrogen chloride and ethynyl ketones were found to undergo rapid isomerization to the trans isomer at 20 °C in the presence of HCl.[5] Since both isomers were isolated from the reaction of $AlCl_3$, acyl chloride, and 3-hexyne, it was postulated that the donor–acceptor complex of $AlCl_3$–acid chloride led to the cis isomer and the more ionic form of this complex was thought to be responsible for the formation of the trans isomer.[4a]

^1H and ^{13}C magnetic resonance spectroscopy have been used to identify and obtain equilibrium constants for the formation of 1:1 and 2:1 complexes of $AlCl_3$ and acetyl chloride in sulfur dioxide solution.[6] Complex formation between $AlCl_3$ and ketones has also been investigated.[7] With this background a 1:1:1 intermediate complex from the Friedel–Crafts reaction of $AlCl_3$, CH_3COCl, and aromatic hydrocarbon was detected under the actual reaction conditions.[8] Therefore it seemed worthwhile to attempt to identify similar intermediates in the acetylation of acetylene.

On the basis of early infrared measurements it was concluded that the complex of acetyl chloride and $SbCl_5$ existed primarily as the ions $CH_3CO^+SbCl_6^-$.[9] This is consistent with a structure obtained by X-ray diffraction[10] but disagrees with later conclusions from infrared[11] and proton resonance spectroscopy.[12] It would appear that the structure of the complex(es) depends upon the state, the solvent, and perhaps the temperature and relative amounts of the reactants. An attempt was made to study the equilibria involved in the $SbCl_5$–acetyl chloride system, and the details of its acetylation of acetylene with the aid of high field NMR.

The proton resonance spectrum of an SO_2 solution of $AlCl_3$, acetyl chloride, and acetylene with a concentration ratio of 1:1:1 taken at −64 °C after the reaction was allowed to proceed for 8 min at 25 °C, has signals from free acetyl chloride, the 1:1 and 2:1 complexes of $AlCl_3$ and acetyl chloride, and the acetyl group from the complex of *trans*-1-chloro-1-buten-3-one and $AlCl_3$. These species, with the exception of the product complex, have been observed at equilibrium in solutions containing only $AlCl_3$ and acetyl chloride[6] and in solutions containing $AlCl_3$, acetyl chloride, and aromatic hydrocarbons.[8] There are also signals from unreacted acetylene and the olefinic protons of the product. The cis isomer is not detected even at longer reaction times. Initial rate data may be interpreted to show that the rate of product formation is directly proportional to the product of the acetylene and $AlCl_3$·CH_3COCl concentrations. Since there is no evidence for an intermediate complex, nor any unusual kinetic behavior, no further details of reaction mechanism can be deduced for this system.

Table I. Lifetime in the System $SbCl_5$–Acetyl Chloride in SO_2

init $SbCl_5$	init CH_3COCl	T °C	$\tau 01^a$	$\tau A2$
0.007 61	0.004 57	−76		
0.007 61	0.004 57	−55	0.1	1.37
0.007 61	0.004 57	−48	0.03	0.45
0.007 61	0.004 57	−33	0.0099	0.20
0.007 61	0.004 57	−21	0.0023	0.17
0.007 61	0.004 57	−8	0.0009	
0.007 61	0.004 57	7		
0.006 19	0.006 58	−76		
0.006 19	0.006 58	−55	0.09	1.37
0.006 19	0.006 58	−43	0.04	0.67
0.006 19	0.006 58	−33	0.013	0.26
0.006 19	0.006 58	−21		
0.006 19	0.006 58	−8	0.0012	
0.006 19	0.006 58	7	0.000 68	

[a] The rate constant $k = 1/\tau$ for these exchanges.

The reaction of $AlCl_3$·CH_3COCl, and $SbCl_5$·CH_3COCl with propyne is much faster than with acetylene, being essentially complete by the time a spectrum is obtained after thawing the sample.

The proton resonance spectrum of an SO_2 solution of $SbCl_5$–acetyl chloride at −76 °C has two signals in the acetyl region, at δ 3.02 and 4.23, and one each at δ 12.09 and 12.76. The signal at δ 4.23 has essentially the same chemical shift as that of the 1:1 acetyl chloride–$AlCl_3$ complex and is assigned to the 1:1 acetyl chloride–$SbCl_5$ complex. Its area does not bear a simple relationship to those of the other signals. The signals at δ 12.76, 12.09 and 3.02 have intensity ratios 1:1:3. The protons at δ 12.76 and 12.09 exchange with each other at a rate which increases with temperature; however their intensity ratio is independent of temperature and of sample composition, provided that acetyl chloride is not in excess. The signal at δ 3.02 is assigned to the methyl group of the diacetylacetylium ion and the signals at δ 12.09 and 12.76 to the hydrogen that is bonded to either carbon or oxygen in its two tautomeric forms.[11] This assignment is consistent with all the rate and equilibrium data and chemical shift measurements to be presented for samples with excess acetyl chloride or with acetylene.

The change in the spectrum for the signals at δ 12.76 and 12.09 by mutual exchange perfectly fits the classical model and was analyzed as such.[13] The rate constants for this exchange are listed in Table I. From their temperature dependence the enthalpy of activation for the exchange is found to be 10.7 ± 0.5 kcal/mol with an essentially zero entropy of activation. A second exchange process which becomes noticeable at higher temperatures is that between the averaged H and CH_3 signals. Approximate rate constants for this exchange, calculated by line broadening,[14] are also listed in Table I. From their temperature dependence the enthalpy and entropy of activation of 7.4 ± 0.7 kcal/mol and −27 ± 3 eu were calculated. With an excess of acetyl chloride the separate signals at δ 12.76 and 12.09 are not observed, but rather a single averaged line is present at δ 12.58.

Samples of $SbCl_5$, acetyl chloride (not in excess), and acetylene also have proton resonance spectra in which the lines normally found at δ 12.76 and 12.09 are averaged to a single broadened line. The degree of acetylation of acetylene was monitored by the decrease in intensity of

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the acetylene signal and the increase in intensity of the product signals relative to neopentane as an inert reference.

It appears that the reaction of acetylene is only with the 1:1 complex since the intensity of the low field signal relative to that of the inert reference does not change during the course of the reaction.

From the totality of these results we may conclude that acetylene forms a weak, labile complex with both the monomeric and trimeric forms of the $SbCl_5 \cdot CH_3COCl$ complex. The compound $SbCl_5 \cdot CH_3COCl \cdot HC{\equiv}CH$ then reacts further to give the final product. No stereochemical information about this ternary complex can be deduced from the present results.

Experimental Section

Chemicals. Aluminum chloride, acetyl chloride, and sulfur dioxide were purified as previously reported.[8] Antimony pentachloride was vacuum distilled into a storage container on the vacuum line. Acetylene, propyne, and neopentane were transferred directly from the supplier's cylinders to storage vessels on the vacuum line or to NMR sample tubes. 4-Chloro-3-penten-2-one was prepared from equilmolar quantities of $AlCl_3$, acetyl chloride, and propyne in CCl_4 at 0 °C. The reaction mixture was decomposed with an ice–water–HCl mixture. After separation the aqueous layer was further extracted with CCl_4. The combined organic layer was washed with water until free of HCl and dried over $CaCl_2$. The solvent was removed and the residue distilled under reduced pressure (bp 74 °C at 7.2 torr). The product was identified, via proton NMR, as 87% *E* and 13% *Z* isomers of 4-chloro-3-penten-2-one.

Sample Preparation. Some $AlCl_3$ was transferred, in a drybox, into an NMR tube closed with a Teflon high vacuum stopcock and weighed. Then the appropriate quantities of sulfur dioxide, neopentane, and acetyl chloride, all measured as vapors, were condensed into the NMR tube. The contents were thawed and mixed, and then the walls of the tubes were washed by distillation of solvent from the solution in the lower part. Finally, a known quantity of the alkyne (also measured as vapor) was condensed into the sample tube, which was then sealed under vacuum. Thawing and mixing of the sample was done in a dry ice–methanol bath. It was immediately transferred to the chilled NMR probe and its spectrum taken at low temperature. A similar procedure was followed with the $SbCl_5$-containing samples except that the $SbCl_5$ was vacuum-transferred and the quantities of all reagents, except acetylene, were verified by weighing the sample tube.

Rate Measurements. Proton and carbon-13 resonance spectra of the $AlCl_3$-containing samples were obtained in the Fourier transform mode on a Varian Associates XL-100 spectrometer equipped with a Nicolet 1180 computer and associated pulsing and power amplifier components. Spectra of the $SbCl_5$-containing samples were obtained with a Bruker AM-400 spectrometer. The variable temperature controllers were calibrated with a methanol sample for each series of spectra. Neopentane, which is inert under the experimental conditions, was used as internal reference and chemical shifts were converted to tetramethylsilane as zero with corrections of δ 0.92 for protons and δ 31.4 for ^{13}C. Concentrations are reported as mole fractions and all calculations are in this unit.

Samples were equilibrated for each reaction period and then the spectra were taken at low temperature as previously described.[8] The concentrations of the various species were calculated from the integrals of their resonance signals and the initial compositions of the samples. Rates of reactions occurring on the NMR time scale were obtained by comparison of spectra at several temperatures with theoretical spectra calculated by a stochastic method.[13]

Registry No. $AlCl_3$, 7446-70-0; antimony pentachloride, 7647-18-9; acetylene, 74-86-2; acetyl chloride, 75-36-5; propyne, 74-99-7; (*E*)-4-chloro-3-penten-2-one, 49784-51-2; (*Z*)-4-chloro-3-penten-2-one, 49784-64-7.

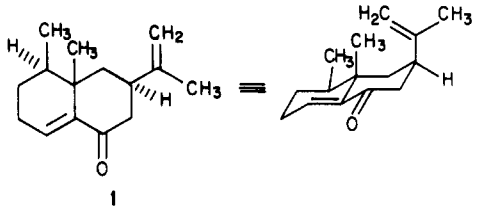
Supplementary Material Available: Proton and carbon-13 chemical shifts for the various species, and characteristic proton resonance spectra (6 pages). Ordering information is given on any current masthead page.

Communications

Stereoselective Insertion of the Isopropenyl Functionality

Summary: A new method of stereoselectively introducing the isopropenyl functionality in the axial orientation on a *trans*-9-methyldecalin ring system by the thermal decomposition of a diazene intermediate is described.

Sir: The isopropenyl moiety can be found widespread throughout terpene chemistry.[1] Classic Wittig methodology applied to methyl ketones can easily generate isopropenyl groups; however, this procedure necessitates the predefined stereochemistry of the precursor.[2] This approach therefore finds most of its utility in the preparation of the more thermodynamically stable products. In certain members of the sesquiterpene class, like the compound eremophilone 1,[3] the isopropenyl group displays an axial orientation on a decalin skeleton. To relieve the 1,3-diaxial



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interaction, eremophilone would be expected to adopt a twist-boat conformation. Several efficient solutions to the problem of producing the less stable isomer have been reported.[4] We have been interested in this problem and the general problem of placing the isopropenyl group in a sterically more hindered position.

Several years ago, Hutchins and co-workers[5] demonstrated that (*p*-tolylsulfonyl)hydrazones of α,β-unsaturated ketones react with $NaBH_3CN$ to produce olefinic products with double-bond migration. The proposed mechanism

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