

reactions in less polar solvents is even less likely.

Experimental Section

Materials. 5-Thiacyclooctanone was synthesized according to the literature.⁸ 5-Bromo-1-pentene was purchased from Aldrich Chemical Co.

5-Methylene-1-thiacyclooctane. The procedure followed was an adaptation of the method developed by Greenwald.⁹ Sodium hydride (4.2 mmol, 0.1 g as a 50% oil dispersion) was placed in a 300-mL three-necked round-bottom flask and washed with three 5-mL portions of pentane to remove the oil. The flask was then fitted with a magnetic stirrer, thermometer, condenser, and septums. The system was evacuated and filled with nitrogen; 3 mL of Me₂SO was added via syringe and the mixture heated for 45 min at 75–80 °C. The flask was then cooled in an ice bath and 1.5 g (4.2 mmol) of methyltriphenylphosphonium bromide dissolved in 8 mL of warm Me₂SO was added. The resulting dark green solution was stirred for 10 min at room temperature. A solution of 0.57 g (4.3 mmol) 5-thiacyclooctanone in 8 mL of Me₂SO was added and the reaction mixture was stirred for an additional 30 min at room temperature. The solution was extracted with pentane, the pentane was removed, and the residue was distilled under reduced pressure: b/p 113 °C (13 mm); yield 0.9 g (50%); ¹H NMR (CDCl₃/Me₄Si) δ 4.85 (s, 2 H), 2.63 (m, 4 H), 2.28 (m, 4 H), 1.91 (m, 4 H); IR (film) ν 3075 cm⁻¹ (=CH₂); mass spectrum (70 eV), *m/z* (reactive intensity) 142 (87, M⁺).

5-(Iodomethyl)-1-thioniabicyclo[3.3.0]octane. To 0.065 g (0.5 mmol) of 5-methylene-1-thiacyclooctane dissolved in 2 mL of methanol was added 0.55 mmol of iodine in methanol dropwise while stirring. The iodine color disappeared immediately. After adding one-third of the iodine a white precipitate formed. The solution became yellow after all the iodine was added and the

solution was stirred for an additional 30 min. The precipitate was removed by suction filtration and washed with 2 mL of methanol. The crystals, which were dried in a desiccator, were suitable for X-ray analysis: mp 120–122 °C. Anal. Calcd for C₈H₁₄I₂S: C, 24.27; H, 3.54. Found: C, 24.57; H, 3.61.

4-Pentenyl Methyl Sulfide. 4-Pentenyl methyl sulfide was synthesized according to the method of Kline,³ but acetonitrile was used instead of ethanol. The final product was purified by gas chromatography. NMR and IR spectra were identical with those in the literature.

Kinetics. Kinetic procedures have been described previously.⁵ The buffered solutions contained invariant concentrations of KI and KCl, balanced so that the total molarity of salts was 1.0. At the concentrations used, >99% of the iodine was consumed at 10 half-lives. The decay of [I₃⁻] at 353 nm in solutions containing an excess of alkene was monitored on a Beckman DU quartz monochromator equipped with a Gilford Instrument 2415A automatic curvette positioner, 252 photometer, and 6051 recorder. The cells were thermostated at 26.0 ± 0.1 °C. The stopped-flow kinetic data were obtained on a Durrum Model 110 spectrophotometer and the output was displayed on a Tektronix 5103N single-beam storage oscilloscope. Reaction time courses were recorded photographically with a Tektronix C-50 oscilloscope camera. The syringes, mixing chamber, and cells were thermostated at 25.0 ± 0.1 °C. A Brinkmann Instrument Lauda type K-2R constant temperature circulator was used on both instruments.

Acknowledgment. We wish to thank Dr. M. M. Olmstead for determining the crystal structure and Dr. John Whittaker, Department of Food Science and Technology U.C. Davis, for the use of the stopped-flow spectrophotometer.

Registry No. 1, 96096-00-3; 5-methylene-1-thiacyclooctane, 96095-99-7; methyltriphenylphosphonium bromide, 1779-49-3; 5-thiacyclooctanone, 20701-80-8; 4-pentenyl methyl sulfide, 69632-05-9.

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Dichlorocarbene from Flash Vacuum Pyrolysis of Trimethyl(trichloromethyl)silane. Possible Observation of 1,1-Dichloro 3-Phenyl Carbonyl Ylide

John F. Gisch and John A. Landgrebe*

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

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Flash vacuum pyrolysis of trimethyl(trichloromethyl)silane **3** at 500–700 °C was shown to be a simple and efficient method for the production of :CCl₂ in the gas phase. The copyrolysis of silane **3** and benzaldehyde (**7**) at 600 °C led to 1,1,1-trichloro-2-phenyl-2-(trimethylsiloxy)ethane (**8**), a 1:1 adduct, in addition to benzal chloride (**15**) and α-chlorophenylacetyl chloride (**16**), products thought to arise from 1,1-dichloro 3-phenyl carbonyl ylide **17** as outlined in Scheme I. An orange-red material trapped at 77 K could be photobleached as well as thermally bleached and had an IR band at 1650 cm⁻¹ and a significant absorption with λ_{max} 510 nm (and a broad shoulder at 580 nm).

Dihalo carbonyl ylides **1** have been implicated as key intermediates required to explain the variety of chemical reactions which take place when appropriate phenyl(trihalomethyl)mercurials are thermally decomposed in benzene in the presence of aromatic and aliphatic aldehydes and ketones.¹⁻³ We now report a convenient pre-

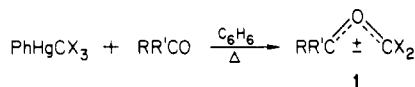
cursor for the generation of ¹A₁ :CCl₂ in the gas phase and its use in the preparation of a trapped species with chem-

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(2) (a) Gill, H. S.; Landgrebe, J. A. *J. Org. Chem.* 1983, 48, 1051. (b) Gill, H. S.; Landgrebe, J. A. *Tetrahedron Lett.* 1982, 23, 5099. (c) Martin, C. W.; Lund, P. R.; Rapp, E.; Landgrebe, J. A. *J. Org. Chem.* 1978, 43, 1071. (d) Martin, C. W.; Landgrebe, J. A.; Rapp, E. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 326. (e) Martin, C. W.; Landgrebe, J. A.; Rapp, E. *J. Chem. Soc., Chem. Commun.* 1971, 1438.

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ical and spectral characteristics which could be associated with 1,1-dichloro 3-phenyl carbonyl ylide 1 ($R = Ph, R' = H, X = Cl$).



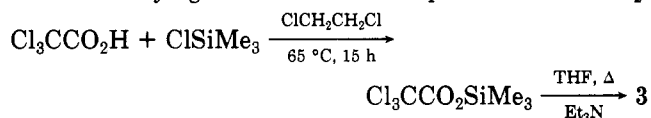
Results and Discussion

Trimethyl(trichloromethyl)silane (3). Although $:\text{CCl}_2$ has been generated by the gas-phase pyrolysis of both carbon tetrachloride⁴ and chloroform^{4a,5,6} at 400–1500 °C, these precursors result in substantial amounts of free radicals and other byproducts which are sometimes undesirable. Similar problems have been noted in the gas-phase pyrolyses of (trichloromethyl)mercury derivatives at 220–550 °C, even though matrix isolation of the resulting fragments at 5–15 K in argon provided useful infrared data on $^1\text{A}_1 : \text{CCl}_2$.⁷ The flash vacuum pyrolysis (FVP) of reactive, liquid trichloro(trichloromethyl)silane (2) produces

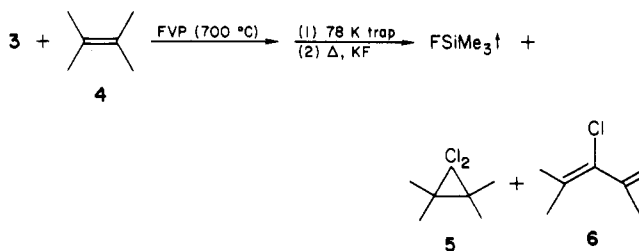
$$\text{Cl}_3\text{SiCCl}_3 \quad \text{Me}_3\text{SiCCl}_3 \quad 3$$

SiCl_4 in addition to $:\text{CCl}_2$.^{8,9} Therefore the unreported but analogous decomposition of trimethyl(trichloromethyl)silane (3), a stable crystalline solid, was explored. The trimethylsilyl leaving group has been employed recently for the generation of various carbenes under FVP conditions,^{9–12} and the efficient production of $:\text{CCl}_2$ from silane 3 in solution in the presence of fluoride ion at 25 °C has been published.¹³

Because syntheses of silane 3 by Spier¹⁴ and by Bamford and Pant¹⁵ were reported to give low yields or had difficult work ups, the method of Hergott and Simchen¹⁶ was employed as shown, but with careful extraction of all of the triethylamine from the crude product prior to sublimation¹⁷ and drying of the sublimate in pentane with CaH_2 .

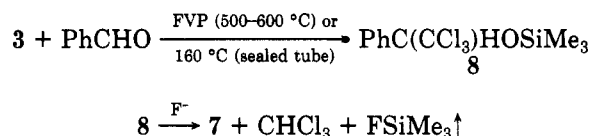


The efficacy of silane 3 as a convenient source of $:\text{CCl}_2$ was tested by decomposing a mixture of 3 and 2,3-dimethyl-2-butene (4) under FVP conditions at 700 °C (10^{-3} – 10^{-4} torr and 0.1 mmol/min flow). Condensation of the effluent vapors at 78 K followed by gradual warming

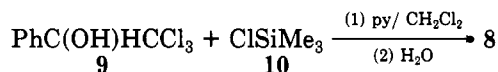


of the condensate at 1 atm until it drops onto excess KF ¹⁸ resulted in the formation of a 62–72% combined yield of dichlorocarbene adduct 5 and chlorodiene 6. The latter compound was derived from the thermal rearrangement of 5 followed by loss of HCl .^{5a,19,20} The ratio of 5 to 6 was about 1:20. No appreciable decomposition of 3 occurred below 500 °C. Confirmation of the presence of $:\text{CCl}_2$ during the pyrolysis of silane 3 under comparable FVP conditions was made by Harmony, Predmore, and Murray²¹ who observed that the laser-induced fluorescence excitation spectrum from the $^1\text{B}_1$ excited state of the $:\text{CCl}_2$ was in general agreement with that reported by Tiee, Wampler, and Rice.²²

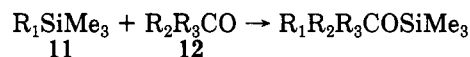
1,1,1-Trichloro-2-phenyl-2-(trimethylsiloxy)ethane (8). Copyrolysis of a 1:5 mole ratio of silane 3 and benzaldehyde (7) under FVP conditions at 500–600 °C resulted



in silyl ether 8 as 70–90% of the GC volatile materials produced. The same product was isolated in 77% yield when silane 3 and aldehyde 7 were heated in a sealed tube at 160 °C. Treatment of silyl ether 8 with KF in acetonitrile resulted in benzaldehyde, chloroform, and presumably fluorotrimethylsilane. The identification of 8 was confirmed when it was shown that the MS, ^1H NMR, and ^{13}C NMR spectra were identical with those of the product from the treatment of phenyl(trichloromethyl)carbinol (9)



with chlorotrimethylsilane (10). The production of 8 is analogous to the observed addition of silanes 11 to various aldehydes and ketones 12, where $\text{R}_1 = \text{CH}_2\text{CN}$,²³ $\text{CH}_2\text{CO}_2\text{Et}$,²³ N_3 ,²⁴ NRCOR' ,²⁵ pyridyl,²⁶ C_6X_5 ($\text{X} = \text{Cl, F}$),²⁷ CN ,²⁸ NR_2 ,²⁹ and SR .³⁰



(18) Although treatment with KF is not essential, it serves to convert the chlorotrimethylsilane produced in the pyrolysis of silane 3 to gaseous fluorotrimethylsilane.

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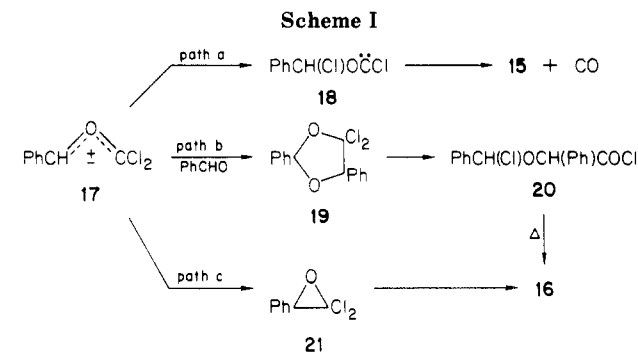
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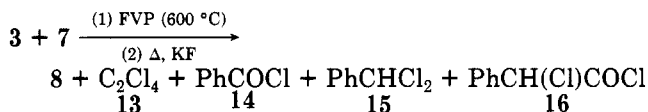
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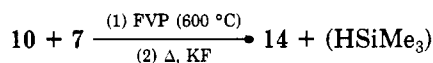
(17) The presence of even traces of triethylamine in purified silane 3 resulted in yellow discoloration over a period of days.



1,1-Dichloro 3-Phenyl Carbonyl Ylide (17). In addition to silyl ether 8, the copyrolysis of silane 3, with benzaldehyde resulted in the formation of much smaller amounts of tetrachloroethylene (13), a common byproduct



of $:\text{CCl}_2$ formation, benzoyl chloride (14), benzal chloride (15), and α -chlorophenylacetyl chloride (16), which were identified by GC-MS comparisons with authentic samples.³¹ Although the origin of the benzoyl chloride (14) is not entirely certain, it was shown to be a product of the FVP of chlorotrimethylsilane (10), which is present in significant amounts during the pyrolysis of silane 3 and benzaldehyde (7) at 600 °C.



Of greater interest are dichloride 15 and chloroacetyl chloride 16, which are products anticipated from the production of 1,1-dichloro 3-phenyl carbonyl ylide 17.² Previous studies have shown that when ylide 17 was generated in benzene at 80 °C by the thermal decomposition of phenyl(bromodichloromethyl)mercury in the presence of benzaldehyde, the observed products consisted of dichloride 15, CO, and acid chloride 20, as outlined by paths a and b of Scheme I.² Acid chloride 14 was not observed other than in trace amounts. The presence of significant amounts of chloroacetyl chloride 16 under the FVP conditions of the current study can be rationalized by the breakdown of acid chloride 20³² and/or the electrocyclic closure of ylide 17 to dichlorooxirane 21 followed by rearrangement of 21 to 16, the latter reaction known to be quite facile.³³ Although extreme difficulties were encountered in attempts to determine absolute yields, the ratio of dichloride 15 to chloroacetyl chloride 16 was about 1:6 when silane 3 and benzaldehyde were copyrolyzed at 600 °C.³⁴

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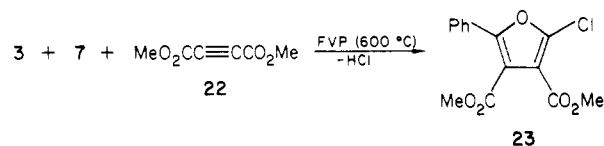
(31) Very small amounts of α,β,β -trichlorostyrene were also observed and presumed to be the result of $:\text{CCl}_2$ attack on dichloride 15 followed by loss of HCl.

(32) Acid chloride 20 has resisted attempts to isolate it, but is known to convert to acid chloride 16 under acid-catalyzed conditions and does not appear to survive gas chromatography;² unpublished observations of C. W. Martin.

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Consistent with other reports of the photobleaching of carbonyl ylides,³⁵ the orange-red color of the frozen pyrolyzate was quickly (2–3 min) bleached by irradiation with a quartz halogen lamp at a distance of 6 cm from the cold finger, or more slowly (ca. 1 h) by ambient light.³⁶ The product mixture after photobleaching favored chloroacetyl chloride 16 over dichloride 15, as in the entirely thermal reaction described previously.

As an additional chemical test for the presence of ylide 17, the copyrolysis of silane 3 with an excess of aldehyde 7 and dimethyl acetylenedicarboxylic (22) at 600 °C resulted in the formation of furan 23, identified by GC-MS comparison with an authentic sample.^{2a,b} These results were completely analogous to those obtained from the decomposition of phenyl(bromodichloromethyl)mercury in the presence of aldehyde 7 and acetylene 22 in benzene at 80 °C.^{2a,b} The efficiency by which ylide 17 was trapped by acetylene 22 was evidenced by the absence of either dichloride 15 or chloroacetyl chloride 16 among the pyrolysis products.



An IR spectrum at 77 K of the orange-red pyrolyzate from the FVP of silane 3 and aldehyde 7 at 500 °C showed an intense, broad band at 1650 cm^{-1} which was completely absent in the control pyrolyses of either 3 or 7 alone, and absent from silyl ether 8. As the pyrolyzate was warmed, both the visible color and the IR band disappeared in qualitatively the same time. Although the band could be associated with a C–O stretching mode in ylide 17, which would be expected to have a lower bond order and corresponding lower stretching frequency than in the aldehyde precursor, conclusive proof for that assignment is lacking. The only previously reported infrared data on a carbonyl ylide are those of Milligan and Jacox³⁷ for the ylide derived from the reaction of methylene with carbon dioxide. Among the bands they reported was one at 1893–1900 cm^{-1} believed to be associated with a C–O stretching vibration and substantially less than the value of 2349 cm^{-1} for CO_2 .³⁸

A UV-vis spectrum of the orange-red material at 77 K displayed a significant absorption with λ_{max} 510 nm and a broad shoulder at 580 nm fully consistent with the data reported on other phenyl-substituted carbonyl ylides.^{35,39}

(34) Introduction of the benzaldehyde immediately after the hot zone changed the ratio of 15:16 to 12:1. Under such conditions ylide 17 would be quickly trapped at low temperature. If path c were not an important source of 16, path a, which is unimolecular, might be expected to dominate over path b as the matrix was warmed.

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(36) A control pyrolysis of silane 3 and benzaldehyde at 400 °C produced a colorless pyrolyzate, but about the same amount of silyl ether 8 as in the pyrolyses at higher temperatures, which indicates that the orange-red color was not associated with the reaction to form silyl ether 8.

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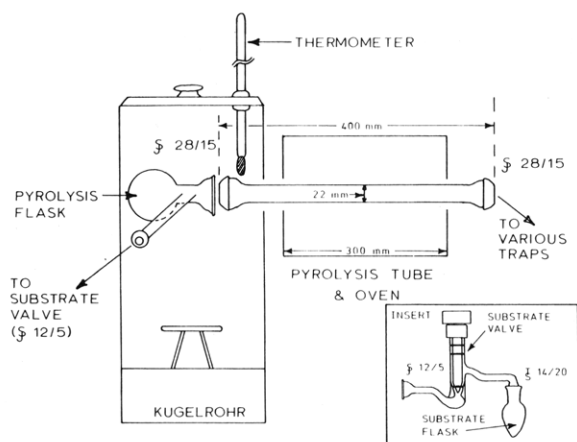


Figure 1. Flash vacuum pyrolysis apparatus.

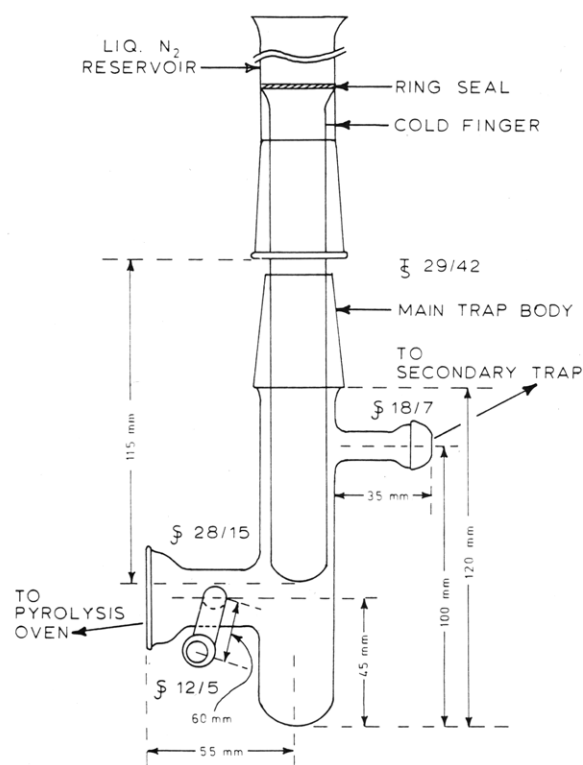


Figure 2. Cold finger trap.

However, conclusions regarding any of the spectral assignments must remain tentative.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. ^1H NMR spectra were determined with a 60-MHz Varian EM-360, 80-MHz Bruker WP-80FT, or 90-MHz Perkin-Elmer R-32 spectrometer. MS and GC/MS data were obtained on a Ribermag R10-10 quadrupole mass spectrometer fitted with a 25-m OV-101 capillary column and interfaced to a PDP-8A computer. Precise mass determinations were made by peak matching on a Varian MAT CH-5 magnetic sector mass spectrometer interfaced to a PDP-8A computer. Infrared data were recorded with a Beckman IR-8, Beckman Acculab3, or IBM FTIR-32 spectrophotometer. A Perkin-Elmer 555 or Lambda 5 spectrophotometer was used to obtain ultraviolet-visible spectra.

GC analyses were accomplished with a Perkin-Elmer Sigma 3B instrument attached to a Hewlett-Packard 3390A recording integrator. Columns used included 3% OV-101 or 10% Carbowax 20M on 80/100 Chromosorb W-HP (both 6 ft \times $1/8$ in.) and an OV-101 capillary column (25 m). HPLC analyses were performed on a Perkin-Elmer Series 3 liquid chromatograph with Whatman

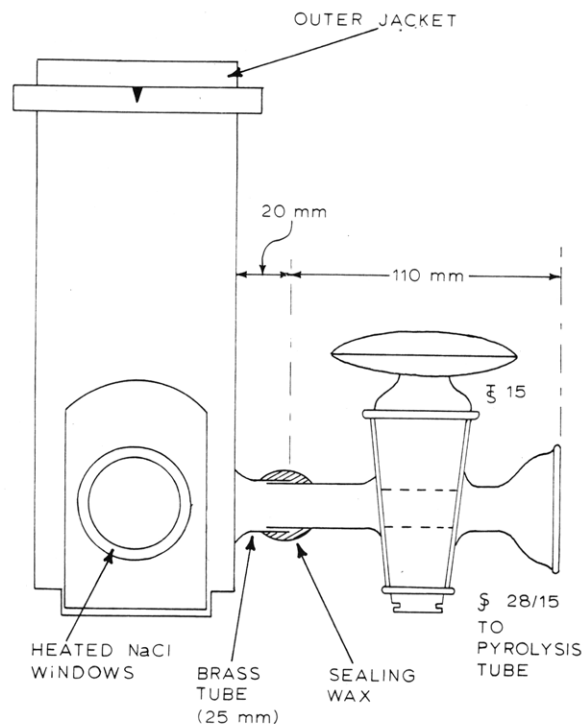


Figure 3. Modified low-temperature cell.

Partisil PXS 10/25 ODS-2 reverse-phase column and Perkin-Elmer LC-55B spectrophotometric detector. TLC was done on silica gel 60F-254 sheets from E. Merck.

Flash Vacuum Pyrolyses. The apparatus shown in Figure 1 was connected to a cold-finger trap (Figure 2) and a secondary trap which led to a vacuum line. An unpacked Vycor pyrolysis tube was used. The cold surface of the first trap was ca. 5 cm beyond the end of the hot zone. Normally ca. 58 mg (0.3 mmol) of silane 3 was placed into the pyrolysis flask, and when used, ca. 250 mg of a substrate was placed in the substrate flask. Potassium fluoride (ca. 200 mg) was added to the bottom of the cold finger trap. While the silane and substrate were cooled with liquid N_2 (substrate needle valve open), the system was evacuated, the cold finger and secondary traps were filled with liquid N_2 , the needle valve was closed, and the cold baths removed from the pyrolysis and substrate flasks. With the Kugelrohr heating unit at 60–110 $^\circ\text{C}$ and the pyrolysis tube at 500–700 $^\circ\text{C}$, substrate was metered into the system while silane 3 sublimed through the hot zone.

After the system was vented and the liquid N_2 blown from the cold finger, any pyrolyzate remaining on the cold finger was rinsed onto the KF with solvent and subjected to chromatographic and spectroscopic analyses. The frozen pyrolyzate was normally colorless except when benzaldehyde was used as the substrate; the color was then light orange-red and disappeared upon warming to room temperature.

Low-temperature IR and UV-vis spectra were obtained by use of a modified Research and Industrial Instruments Co. (RIIC) VLT-2 variable temperature IR cell and TEM-1 temperature controller. Modifications shown in Figure 3 included the addition of a 15-mm straight bore high-vacuum stopcock with 28/15 spherical joint and 25-mm brass fitting to the outer metal jacket. The cell holder (Figure 4) heater assemblies were disconnected, and the cell holder was fitted with a NaCl plate (3 mm thick) with a hole drilled 5 mm from the edge to accommodate a Chromel-Alumel thermocouple. Jacket window heaters were wired in series and connected to the controller. After the jacket window heaters had been on for 15 min, liquid N_2 was transferred to the well and allowed to equilibrate the cell at 77 K for 30 min before each pyrolysis experiment. Spectra were obtained by closing the stopcock and rotating the cell 90 $^\circ$ in the holder.

Quantitative Determination of Dichlorocarbene-Derived Products. After copyrolysis of silane 3 and alkene 4, the system was repressurized, the trap disconnected, and liquid N_2 blown from the cold finger. The pyrolyzate was allowed to drop onto

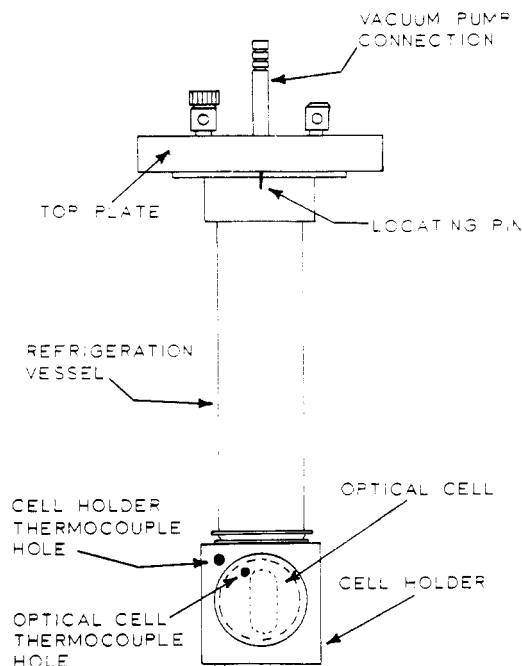


Figure 4. Cell holder assembly.

anhydrous KF, swirled, and filtered through a glass wool plug into a vial. *o*-Dichlorobenzene (ca. 20 mg, distilled from CaH₂ and stored over 4 Å molecular sieves) was added as an internal standard.

GC detector response was calibrated by injection of solutions containing internal standard, cyclopropane **5**, and chloro diene **6** in known and varied quantities followed by linear regression analysis in order to provide correlation of peak area ratios with compounds weight ratios. Each analysis was determined from an average of the results from three injections (1 μL) on 3% OV-101 (70°).

Trimethylsilyl trichloroacetate was prepared by the method of Hergott and Simchen¹⁶ to give a colorless liquid in 66.8% yield based on starting acid: bp 80–82 °C (20 torr) (lit.¹⁶ bp 69 °C (10 torr)); ¹H NMR (CCl₄, dioxane) δ 0.32 (s).

Trimethyl(trichloromethyl)silane (3) was prepared by a modification of the procedure of Hergott and Simchen.¹⁶ Trimethylsilyl trichloroacetate (47.2 g, 0.2 mol) and triethylamine (4.2 g, 0.04 mol, distilled from CaH₂) in THF (100 mL, distilled from LiAlH₄) were stirred under argon for 4 h at 67 °C during which time CO₂ was evolved. After the THF was distilled, the residue was dissolved in pentane, washed with 1 N HCl and water (3 X), dried with CaSO₄, filtered, and evaporated cold. The white solid was sublimed at 70 °C (20 torr) to give white hygroscopic needles (18.6 g, 0.097 mol, 48.6% yield) with mp 130–132 °C (closed capillary) (lit.¹⁶ mp 130–132 °C): ¹H NMR (CCl₄) δ 0.39 (s); ¹³C NMR (C₆D₆) δ 95.88 (s), -4.07 (q); IR (CDCl₃) 2985, 2919, 1418, 1414, 1258, 890, 855, 812, 689 cm⁻¹; MS (70 eV), *m/e* (relative

intensity) 113 (35.2, Cl₂), 93 (13.6, Cl), 73 (100), 45 (16.9).⁴⁰

1,1,1-Trichloro-2-phenyl-2-(trimethylsiloxy)ethane (8). Phenyl(trichloromethyl)carbinol (**9**) was prepared by C. W. Martin⁴¹ according to the procedure of Reeve and Fine⁴² and purified by fractional distillation, bp 170 °C (40 torr), (lit.⁴² bp 148 °C 16 torr). Chlorotrimethylsilane (1.92 g, 2.26 mL, 17.8 mmol) was added dropwise (10 min, stirring, argon) to the carbinol (2.0 g, 8.9 mmol) and pyridine (1.40 g, 17.8 mmol) in dry CH₂Cl₂. After 1 h of additional stirring, a white flocculent precipitate appeared. The cold reaction mixture (ice bath) was washed with ice water (50 mL), cold 3 N HCl (2 × 50 mL), and cold saturated sodium bicarbonate solution (50 mL). The organic layer was dried (CaSO₄), evaporated (crude yield 67%), and distilled (5 cm wire spiral column) to give a colorless liquid (0.9 g, 3.0 mmol, 35% yield): bp 148–51 °C (19 torr); ¹H NMR (CCl₄, dioxane internal standard) δ 7.7–7.4 (m, 2 H), 7.4–7.2 (m, 3 H), 5.02 (s, 1 H), 0.08 (s, 9 H); ¹³C NMR (CDCl₃) δ 137.22 (s), 129.64 (d), 129.21 (d), 127.69 (d), 102.93 (s), 85.27 (d), 0.07 (q); IR (neat) 3110, 3090, 3060, 2980, 2910, 1495, 1450, 1410, 1350, 1320, 1255, 1200, 1120 (br), 1080, 920, 885 (br), 780, 755, 743, 700, 650, 610 cm⁻¹; MS (70 eV), *m/e* (relative intensity) 296 (M⁺, 0.5), 179 (100), 125 (52.0, Cl), 107 (10.7), 105 (12.5), 93 (13.0, Cl), 77 (11.2), 73 (94.6), 45 (11.6); MS (CI, NH₃) gave an isotope cluster at 207, 209, 211 (M⁺ - Me₃SiO); MS (negative ion, NH₃) showed a strong isotope cluster at *m/e* 117, 119, 121 (CCl₃). Precise *m/e* calcd for C₁₀H₁₅OSi (M⁺ - CCl₃) 179.089, found 179.089 ± 0.001.

Anal. Calcd for C₁₁H₁₅Cl₃OSi: C, 44.38; H, 5.08. Found: C, 44.09; H, 5.10.

Although purified silyl ether **8** was quite stable, **8** mixed with the various acid and alkyl chlorides present after FVP of silane **3** and benzaldehyde was slowly converted (7–10 days) to an isomeric compound which was not completely identified: ¹H NMR (CCl₄, dioxane internal standard) δ 0.22 (s, 1 H), 5.20 (s, 1 H), 7.45–7.20 (m, 3 H), 7.70–7.45 (m, 2 H); ¹³C NMR⁴³ (CDCl₃) δ 2.1 (q), 84.7 (d), 103.3 (d), 128.0 (d), 129.4 (d), 135.0 (s); MS (70 eV), *m/e* (relative intensity) 296 (M⁺, 1.0), 179 (100), 125 (52.3, 1 Cl), 107 (58.7), 93 (13.3), 79 (37.4), 77 (21.3), 73 (98.5).

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Registry No. 1 (R = Ph, R' = H, X = Cl), 96363-61-0; 3, 5936-98-1; 4, 563-79-1; 5, 3141-45-5; 6, 1809-75-2; 7, 100-52-7; 8, 54034-90-1; 9, 2000-43-3; 13, 127-18-4; 14, 98-88-4; 15, 98-87-3; 16, 2912-62-1; 22, 762-42-5; 23, 84681-08-3; CH₃C(O)OSiMe₃, 25436-07-1; Et₃N, 121-44-8; Me₃SiCl, 75-77-4; Me₃SiF, 420-56-4; Cl₂C, 1605-72-7.

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(43) One of the carbon signals could not be located even though its presence was clearly indicated from the MS data.