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COPYROLYSIS OF 1,1-DIMETHYL-1-SILACYCLOBUTANE AND ACROLEIN

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Summary

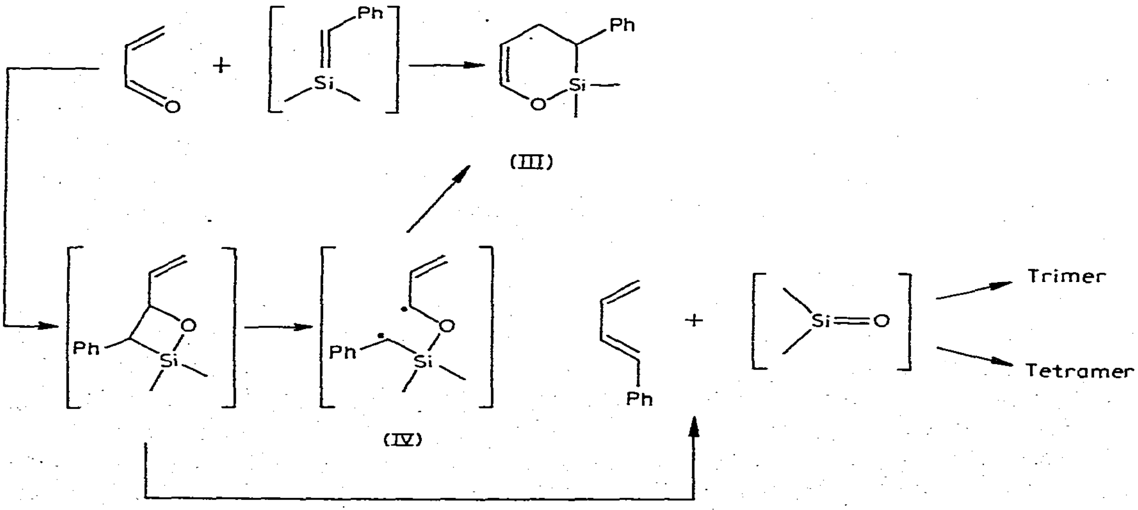
Copyrolysis of 1,1-dimethyl-1-silacyclobutane and acrolein at 600°C in the gas phase yields ethylene, hexamethylcyclotrisiloxane (trimer), octamethylcyclotetrasiloxane (tetramer), 1,3-butadiene, 3-cyclohexene-1-carboxaldehyde, 1,1-dimethyl-2-oxa-1-sila-3-cyclohexene, and 1,1,3,3-tetramethyl-2,4-dioxa-1,3-disila-5-cyclooctene. Formation of the products can be accounted for in terms of initial competing [2+2] and [2+4] cycloaddition reactions between acrolein and [$(CH_3)_2Si{=}CH_2$] (formed by pyrolysis of 1,1-dimethyl-1-silacyclobutane). The [2+4] reaction yields 1,1-dimethyl-2-oxa-1-sila-3-cyclohexene. The [2+2] reaction yields an unstable silaoxetane intermediate which decomposes to yield 1,3-butadiene and dimethylsilanone [$(CH_3)_2Si{=}O$]. Cyclooligomerization of the reactive dimethylsilanone yields trimer and tetramer. Insertion of dimethylsilanone into the Si—O single bond of 1,1-dimethyl-2-oxa-1-sila-3-cyclohexene yields 1,1,3,3-tetramethyl-2,4-dioxa-1,3-disila-5-cyclooctene. 3-Cyclohexene-1-carboxaldehyde is formed by a Diels—Alder reaction between 1,3-butadiene and excess acrolein under the reaction conditions.

There has been considerable recent interest in the reaction of intermediates possessing a formal carbon—silicon double bond [1-7]. Such intermediates may be generated by pyrolysis of silacyclobutanes [8-11]. Several pieces of evidence suggest that these intermediates posses significant zwitterionic character [$(CH_3)_2Si^{\delta+}{-}CH_2^{\delta-}$]. Thus, pyrolysis of 1,1-dimethyl-1-silacyclobutane (I) in the gas phase yields ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane, the head to tail dimer of two methylenedimethylsilane [$CH_2{=}Si(CH_3)_2$] (II) intermediates [8-10]. This exclusive formation of head-to-tail dimer may be due to the polar nature of II. Copyrolysis of I with benzophenone leads to 1,1-diphenylethylene, hexamethylcyclotrisiloxane (trimer) and octamethylcyclotetrasiloxane (tetramer) [3,6], probably by the following reaction sequence. A [2+2] cycloaddition of II and the ketone yields an unstable silaoxetane which decomposes to yield an olefin and dimethylsilanone [$(CH_3)_2Si{=}O$]. The latter, then undergoes cyclooligomerization to yield trimer and tetramer [5]. Analogous [2+2] cycloaddition reactions between II and added alkenes (to yield new silacyclobutanes) [10,12] and imines (to yield alkenes and cyclodisilazanes) have been observed [7].

On the other hand, copyrolysis of I with 1,3-dienes yields 1,1-dimethyl-1-sila-3-cyclohexenes and ethylene. Formation of the former can be explained by a [2+4] cycloaddition reaction between II and the 1,3-diene [13,14].

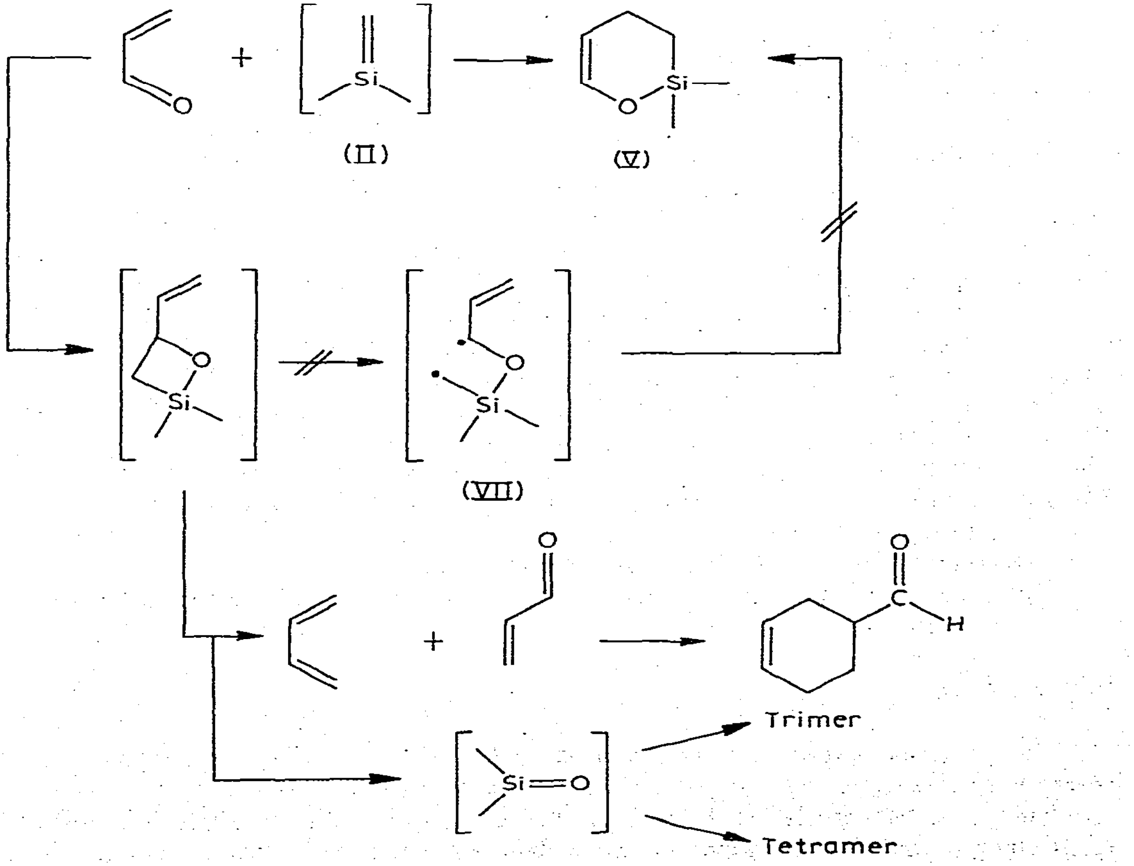
We have reported previously that copyrolysis of 1,1-dimethyl-2-phenyl-1-silacyclobutane and acrolein at 500°C and atmospheric pressure in a flow pyrolysis system with purified nitrogen as the carrier gas leads to products which could be rationalized in terms of competing [2+2] and [2+4] cycloaddition reactions between the phenyl-substituted carbon—silicon double bonded intermediate and acrolein [15]. Thus 1,2-dihydronaphthalene, naphthalene, trimer, and tetramer may be formed by an initial [2+2] cycloaddition reaction. 1,2-Dihydronaphthalene and naphthalene have been shown to be secondary products formed from 1-phenyl-1,3-butadiene under the reaction conditions, but formation of 1,1-dimethyl-2-oxa-6-phenyl-1-sila-3-cyclohexene (III) may be accounted for by a direct [2+4] cycloaddition reaction. However, an alternative possibility exists, namely that the initial silaoxetane adduct formed by [2+2] cycloaddition may undergo carbon—carbon bond scission to yield an allylic—benzylic radical pair (IV) which recombines to yield III in competition with the fragmentation which yields 1-phenyl-1,3-butadiene and dimethylsilanone (Scheme 1).

SCHEME 1. REACTION OF ACROLEIN WITH [$PhCH{=}Si(CH_3)_2$].



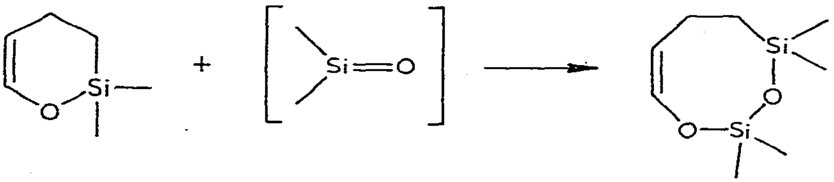
An attempt to distinguish between these two possibilities seemed worthwhile since few cycloaddition reactions are known in which [2+2] and [2+4] pathways are competitive [16-20]. For this reason, the copyrolysis of I with acrolein was studied at 600°C and atmospheric pressure in a flow pyrolysis apparatus with purified nitrogen as the carrier gas. (The higher temperature was required to decompose I). The products formed in this reaction were: ethylene, 1,3-butadiene, 3-cyclohexene-1-carboxaldehyde [21], trimer, tetramer, 1,1-dimethyl-2-oxa-1-sila-3-cyclohexene (V), 1,1,3,3-tetramethyl-2,4-dioxa-1,3-disila-5-cyclooctene (VI). Formation of trimer, tetramer, and 1,3-butadiene is expected from the decomposition of an initial [2+2] silaoxetane intermediate. Under the reaction conditions 1,3-butadiene is partially trapped in a Diels—Alder reaction with excess acrolein to yield 3-cyclohexene-1-carboxaldehyde [21]. On the other hand, V is probably formed by a [2+4] cycloaddition reaction between II and acrolein. Formation of V in comparable yield (15.5%) to III (16.6%) from the reaction of 1,1-dimethyl-2-phenyl-1-silacyclobutane and acrolein is inconsistent with the other mechanistic possibility. Thus scission of the carbon—carbon bond of the silaoxetane intermediate formed by [2+2] reaction of $[(CH_3)_2Si{=}CHPh]$ with acrolein would lead to IV, while scission of the carbon—carbon bond of the silaoxetane intermediate formed by [2+2] reaction of II with acrolein would lead to an allylic-primary alkyl radical pair (VII). The radical pair VII is certainly less favorable than the radical pair IV (Scheme 2).

SCHEME 2. REACTION OF $[(CH_3)_2Si{=}CH_2]$ WITH ACROLEIN



Finally, VI (8.7%) probably is formed by insertion of dimethylsilanone into the silicon—oxygen single bond of V (Reaction III). Thus the initial yield of V is probably 24.2% = 15.5% + 8.7%. This makes the argument for the [2+4] reaction pathway even stronger. The reverse of several related reactions have been reported [22,23]. Thus, pyrolysis of tetramer initially yields trimer and dimethylsilanone which reacts with excess tetramer to yield pentamer [24]. The reaction forming VI is probably the microscopic reverse of these reactions (Scheme 3). It is usually observed that the trimer is more stable at high temperatures than the tetramer. This is consistent with our observation that on pyrolysis at 625°C the ratio of V to VI was higher but the yield of V + VI was the same.

SCHEME 3. REACTION OF V WITH [$(CH_3)_2Si{=}O$].



(V)

(VI)

A small amount (5%) of the acrolein is pyrolyzed to yield ethylene and carbon monoxide under the reaction conditions [25,26].

The material balance in this reaction is quite good for a high temperature pyrolysis. Thus of 3 g of I pyrolyzed 1 g was not decomposed and was recovered All yields are corrected. The initial products of the [2+2] reaction are 1,3-butadiene and dimethylsilanone. 1,3-Butadiene was not determined directly, but was trapped by reaction with bromine to yield 1,2,3,4-tetrabromobutane (55%) and with acrolein to yield 3-cyclohexene-1-carboxaldehyde (7%). The dimethylsilanone is found in trimer (21.2%), tetramer (17.6%) and VI (8.7%). The products of dimethylsilanone thus account for 47.5%, compared to 62% for 1,3-butadiene products. However, higher siloxane oligomers were present (by GLC) in small amounts but were not identified. The [2+4] cycloaddition products: V (15.5%) and VI (8.7%) equal 24.2%. Thus the products isolated and identified account for 86% (24.2% + 62% based on 1,3-butadiene) of the starting material pyrolyzed. The ratio of [2+2] to [2+4] pathways is approximately 3/1. This is similar to the 4/1 found in the reaction of [$(CH_3)_2Si{=}CHPh$] with acrolein, although the material balance in this case was not as good [15].

In conclusion, we believe these results favor competing [2+2] and [2+4] cycloaddition pathways.

Experimental

Infrared spectra were obtained on a Perkin—Elmer 337 spectrometer and were calibrated against known bands in a polystyrene film. NMR spectra were recorded on a Varian HA-100 spectrometer with methylene chloride (δ 5.28) as internal standard. Mass spectra were obtained on a Hitachi—Perkin—Elmer

RMU-6E spectrometer. Conditions used in determination of mass spectra were: source temperature 150°C; solid inlet 50°C; ionizing voltage 70 eV; filament emission 70 μA; target current 50 μA. Vapor phase chromatography was carried out on a Hewlett—Packard F&M 700. Microanalyses were performed by Elek Microanalytical Laboratories. Melting points are uncorrected.

1,1-Dimethyl-1-silacyclobutane (I) was prepared by literature methods and had properties identical with those previously reported [27,28].

Acrolein was purified by redistillation through a 30 cm Vigreux column, b.p. 52.5-53.5°C/760 mm, immediately prior to use.

Copyrolysis of I and acrolein

The pyrolysis was performed using a vertical tube oven. The pyrolysis tube consisted of a 40 cm long Pyrex glass tube (12.5 mm o.d., 9 mm i.d.) packed with 1 cm long species of 3 mm Pyrex tubing. A pressure equalizing addition funnel and a nitrogen inlet were connected to the pyrolysis tube above the oven. The exit of the column was connected to a trap which was immersed in an ice-water bath. The exit of the trap was connected to another trap immersed in an ice-water bath. Gases exiting from this second trap (carbon monoxide, ethylene, 1,3-butadiene, and nitrogen) were passed through a solution of bromine in carbon disulfide. The nitrogen flow rate was adjusted to 0.5 ml/sec, while the pyrolysis column was maintained at 600°C. The temperature was determined by use of a potentiometer and an Iron—Constantan thermocouple. The temperature gradient across the 30 cm long tube furnace was found to be 10°C at 600°C. The entire apparatus was flame dried. A mixture of 3 g (0.03 mol) of I and 16.8 g (0.30 mol) of acrolein was placed in the addition funnel. This mixture was added to the pyrolysis tube at the rate of 1 drop every 5 sec. The addition took 45 minutes to complete. Thus the average residence time in the hot zone is 8 seconds. Upon completion of the addition, the pyrolysis tube was allowed to cool. Then nitrogen was continued through the system in order to flush 1,3-butadiene into the bromide trap solution. The pyrolysis tube was rinsed with 1 ml of diethyl ether. The material from the two ice-water traps was combined. The trap solution of bromine in carbon disulfide was worked up separately. Excess acrolein and diethyl ether were removed from the material isolated from the ice-water traps by distillation through a 30 cm Vigreux column. The residue (5.15 g) was purified by bulb-to-bulb distillation at 0.01 mm. This volatile material (5.0 g) was resolved by preparative GLC (0.25" × 25', 20% polyphenylether on Chromosorb P, at 100°). The following compounds were isolated and identified:

1,1-Dimethyl-1-silacyclobutane. 1 g (33%) was recovered from the reaction mixture [27,28].

Hexamethylcyclotrisiloxane. (21.2% yield). Properties: m.p. 64°C, IR data and GLC retention time were identical with those of an authentic sample [29].

Octamethylcyclotetrasiloxane. (17.6% yield). Properties: IR data and GLC retention time were identical with those of an authentic sample [29].

1,1-Dimethyl-2-oxa-1-sila-3-cyclohexene. (15.5% yield). An analytical sample was obtained by preparative GLC (0.25" × 4', 7% β,β-ODPN on Chromosorb P, at 30°C). NMR (CCl_4): δ 0.12 (s, 6H), 0.68 (t, 2H) *J* 7 Hz, 2.11 (d of d of t, 2H) *J* 4.5 Hz, *J* 7 Hz, *J* 2 Hz, 4.4 (d of t, 1H) *J* 4.5 Hz, *J* 6.5 Hz, 6.17 (d of t, 1H) J 6.5 Hz, J 2 Hz. IR (film): Si—CH_3 1258, Si—O and C—O 1030 and 1148, and C=C 1635 cm^{-1}. Mass spectrum: parent at m/e 128 (45%), P − 15 at m/e 113 (100%). Anal. Found: C, 56.27; H, 9.42. $C_6H_{12}OSi$ calcd.: C, 56.17; H, 9.43%.

1,1,3,3-Tetramethyl-2,4-dioxa-1,3-disila-5-cyclooctene. (8.7% yield). An analytical sample was obtained by preparative GLC (0.25" × 4', 7% β,β-ODPN on Chromosorb P column, at 60°). NMR (CCl_4): δ 0.06 (s, 6H) 0.10 (s, 6H), 0.69 (m, 2H), 2.19 (m, 2H), 4.77 (d of t, 1H) J 6 Hz, J 8 Hz, 6.04 (d, 1H) J 6 Hz. The following decoupling experiments were carried out. Irradiation at 0.69 caused the multiplet at 2.19 to collapse to a doublet, J 8 Hz. Irradiation at 2.19 caused the multiplet at 0.69 to collapse to a singlet and the doublet of triplets at 4.77 to collapse to a doublet, J 6 Hz. Irradiation at 4.77 caused the doublet at 6.04 to collapse to a singlet, and caused a major change in the multiplet at 2.19. Finally, irradiation at 6.04 caused the doublet of triplets at 4.77 to collapse to a triplet J 8 Hz. IR (film): Si—CH_3 1257; Si—O and C—O 1048, 1083, and 1154; C=C 1640 cm^{-1}. Mass spectrum: parent at m/e 202 (7.4%) and P − 15 at m/e 187 (5.0%). Anal. Found: C, 47.33; H, 8.85. $C_8H_{18}O_2Si_2$ calcd.: C, 47.47; H, 8.96%.

3-Cyclohexene-1-carboxaldehyde [21]. (7.0% yield). NMR (CCl_4): δ 1.99 (m, 6H), 5.55 (s, 2H), 9.53 (s, 1H). IR (film): C=O 1720 and C=C 1650 cm^{-1}. Mass spectrum: parent at m/e 110 (base peak).

Work-up of bromine trap solution

Excess bromine was removed by extraction with an aqueous solution of sodium thiosulfate. The carbon disulfide solution was dried and the solvent removed by evaporation under reduced pressure. The residue was redissolved in hot hexane to separate the sulfur formed by the reaction of sodium thiosulfate and bromine. Sulfur is quite soluble in carbon disulfide but not in hexane [30]. After filtration, the hexane was removed by distillation through a 15 cm Vigreux column at atmospheric pressure to leave 10.4 g of residue. Its composition was determined by NMR integration, i.e., the ratio of 1,2-dibromoethane to 1,2,3,4-tetrabromobutane. This was checked by removal of the 1,2-dibromoethane by bulb-to-bulb distillation at 0.01 mm. The weight of residual 1,2,3,4-tetrabromobutane agreed with that previously determined by NMR within 5%.

1,2-Dibromoethane. 6.3 g were obtained. Its NMR spectrum was identical with that of an authentic sample*. On the basis of pyrolysis of 2 g (0.02 mol) of I, we should have obtained 3.76 g of 1,2-dibromoethane. The other 2.54 g of 1,2-dibromoethane (0.0135 mol) must come from pyrolysis of 0.76 g of acrolein to yield ethylene and carbon monoxide [25,26]. No attempt was made to identify or quantitate the carbon monoxide lost.

1,2,3,4-Tetrabromobutane. 4.1 g was isolated as a mixture of *meso-* and *d,l*-1,2,3,4-tetrabromobutane which were not separated. The NMR spectrum was identical to that of an authentic sample prepared by bubbling 1,3-butadiene into bromine in carbon tetrachloride solution. This is equivalent to a 55% yield of 1,3-butadiene based on 0.02 mol of I pyrolyzed.

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* 1,2-Dibromoethane was purchased from Aldrich Co.

Acknowledgements

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