Organic Chemistry of Dichlorosilane. Additions to Conjugated and Unconjugated Diene Systems Followed by Intramolecular Cyclizations

Robert A. Benkeser,* Edward C. Mozdzen, Wayne C. Muench, Robert T. Roche, and Michael P. Siklosi

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received October 18, 1978

The addition of dichlorosilane to both conjugated and unconjugated dienes was studied in the presence of chloroplatinic acid as a catalyst. The mode of addition to conjugated dienes was predominantly by a 1,4 pathway. With unconjugated dienes, addition to a terminal double bond was much faster than to internal double bonds and hence provided a convenient method for the synthesis of alkenyldichlorosilanes. The latter were cyclized in an intramolecular fashion with catalytic amounts of chloroplatinic acid to form novel cyclic and bicyclic silicon-containing heterocycles. In this fashion the very novel 7,7-dichloro-7-silanorbornane was prepared. Nucleophilic displacement reactions on the silicon atom in this novel compound were also studied.

In 1973 we reported on the chloroplatinic acid-catalyzed addition of dichlorosilane to internal olefins.[1] Unlike trichlorosilane, dichlorosilane was found to add directly to internal double bonds of olefin systems affording good yields of internally substituted alkyldichlorosilanes. In the presence of chloroplatinic acid, dichlorosilane was found to add to acetylenes in predominantly a cis manner to give trans products.[2]

In a continuation of the study of dichlorosilane chemistry, it was decided to investigate the chloroplatinic acid-catalyzed additions of dichlorosilane to both conjugated and unconjugated diene systems The mode of addition (1,2 vs. 1,4) in conjugate dienes was of interest, as well as the regiospecificity of addition to unconjugated systems. Finally, it was felt that the alkenyldichlorosilanes which result from addition to dienes might serve as precursors to a variety of hitherto inaccessible cyclic and bicyclic silicon compounds.

Results and Discussion

The mode of addition of dichlorosilane to conjugated dienes was studied using four representative dienes of this type (entries 1, 2, 3, and 5 of Table I). While a variety of products could, in theory, arise from some of these reactions (e.g., an unsymmetrical conjugated diene reacting both in a 1,2 and 1,4 fashion to give cis and trans mixtures), this did not turn out to be the case. An examination of Table I discloses that the predominant mode of addition was by the 1,4 route. In 1,3-butadiene and isoprene only 1,4 adducts were found along with small amounts of cyclic products and diadducts. Unlike other silanes,[3] dichlorosilane did not seem to show much selectivity in its addition to isoprene, since adducts were obtained from 1,4 additions to both sides of this unsymmetrical diene.

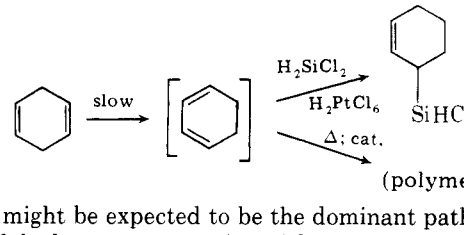
The monoadducts from 1,3-butadiene were characterized by methylation and a comparison of the products with authentic samples synthesized by a different route. The monoadducts from isoprene were also methylated followed by a reduction of the remaining double bond. The latter materials were again identified by comparison with authentic samples.

The addition to 1,3-pentadiene was somewhat more complicated, in that 1,4 addition to both sides of this unsymmetrical diene was observed as well as simple 1,2 addition. Unfortunately, difficulty was encountered in the separation of these isomers even after methylation and hence an accurate isomer distribution was never obtained.

1,3-Cyclohexadiene also gave predominantly 1,4 addition. In this case, the yields of monoadduct were erratic, varying from 30–60%, even when the reactions were seemingly run under identical conditions. The byproduct in this case was a polymeric substance. When the reaction was conducted at room temperature, only polymer was isolated. In a blank experiment, 1,3-cyclohexadiene was heated at 150 °C for 1 h with dichlorosilane and no catalyst. No adduct was obtained, but again considerable polymer was formed.

The addition of dichlorosilane to 1,4-cyclohexadiene gave unexpected results. Instead of the expected 4-dichlorosilylcyclohexene, a mixture of the 3- and 4-dichlorosilylcyclohexene adducts was obtained in a 96:4 ratio. One other product was obtained, either 3- or 4-monochlorocyclohexenylsilane, the compound arising from the addition of monochlorosilane to the diene system.

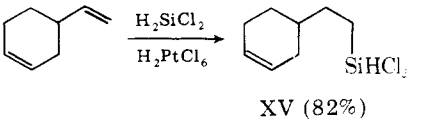
Since the isomer distribution in the case of 1,4-cyclohexadiene was identical to that obtained from 1,3-cyclohexadiene and dichlorosilane, it is likely that isomerization of the 1,4-cyclohexadiene to 1,3-cyclohexadiene took place prior to hydrosilylation. As mentioned previously, even under milder conditions than were used to effect hydrosilylation, 1,3-cyclohexadiene showed a proclivity toward polymerization. One can assume that 1,4-cyclohexadiene could slowly isomerize to the conjugated diene, which would then rapidly undergo hydrosilylation or polymerization, eq 1. Generally, hydrosilylation might be expected to be the dominant pathway because of the large concentration of dichlorosilane relative to the 1,3-cyclohexadiene.



(1)

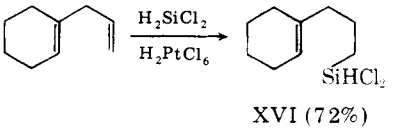
Since no 1-isomer (the expected thermodynamic product) was observed, it is unlikely that isomerization occurred after hydrosilylation. Furthermore, isomerizations as depicted in eq 1 have been observed in similar systems.[4,5]

Addition of dichlorosilane to unconjugated dienes containing one terminal double bond produced terminal adducts in high yields. In both 4-vinylcyclohexene and 1-allylcyclohexene, eq 2 and 3, the double bond in the ring did not isomerize.[6]



(2)

XV (82%)

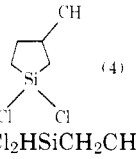
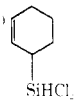
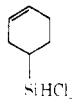
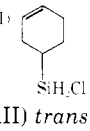
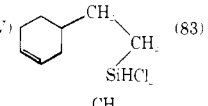
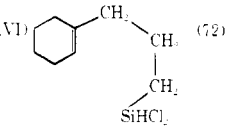


(3)

XVI (72%)

0022-3263/79/1944-1370$01.00/0

Table I. Chloroplatinic Acid Catalyzed Additions of Dichlorosilane to Dienes

diene	registry no.	temp, °C (time, h)	products[a] (% yield)	registry no.
(1) 1,3-butadiene	106-99-0	100 (0.5)	(I) *trans*-$CH_3CH{=}CHCH_2SiHCl_2$[d] (14)	69238-76-2
			(II) *cis*-$CH_3CH{=}CHCH_2SiHCl_2$ (58)	69238-77-3
			(III) $(CH_2)_4SiCl_2$ (3)	2406-33-9
			(IV) $Cl_2HSi(CH_2)_4SiHCl_2$ (2)	69238-78-4
(2) isoprene	78-79-5	100 (0.5)	(V) $(CH_3)_2C{=}CHCH_2SiHCl_2$ } (59)[c]	69238-79-5
			(VI) $CH_3CH{=}C(CH_3)CH_2SiHCl_2$ }	69238-80-8
			(VII)  (4)	69238-81-9
			(VIII) $Cl_2HSiCH_2CH(CH_3)(CH_2)_2SiHCl_2$ (1)	69238-82-0
(3) 1,3-cyclohexadiene	572-57-4	150 (1)	(IX)  (94)[b] } (41)[c]	69238-83-1
			(X)  (6)[b] }	69238-84-2
(4) 1,4-cyclohexadiene	628-41-1	150 (15)	(IX) (94)[b] } (70)[c]	69238-85-3
			(X) (6)[b] }	
			(XI)  (5)	
(5) 1,3-pentadiene	504-60-9	148 (0.5)	(XII) *trans*-$CH_3CH{=}CHCHSiHCl_2CH_3$ (15)	69238-86-4
			(XIII) $CH_3CH_2CH{=}CHCH_2SiHCl_2$ } (33)[c]	69238-87-5
			(XIV) $CH_3CH{=}CH(CH_2)_2SiHCl_2$ }	69238-88-6
(6) 4-vinylcyclohexene	100-40-3	55 (12)	(XV)  (83)	69238-89-7
(7) 1-allylcyclohexene	13511-13-2	75 (21)	(XVI)  (72)	69238-90-0

[a] Satisfactory analytical data (±0.3% for C, H, Si, Cl) were reported for all new compounds listed in this table. [b] This number represents the relative percentage of this isomer which was obtained. [c] This number represents the percent yield of the isomer mixture which was obtained. [d] The NMR data which follow were obtained in a solution of CCl_4–Me_4Si. Compound I: δ 1.72 (d, 3), 2.05 (d, 2), 5.42 (m, 3). II: δ 1.64 (d, 3), 2.13 (d, 2), 5.47 (m, 3). IV: δ 1.28 (m, 4), 1.63 (m, 4), 5.52 (t, 2). V + VI mixture: δ 1.67 (m, 6), 2.08 (m, 2), 5.15 (m, 1) 5.39, and 5.48 (t, 1). VII: δ 0.4–2.2 (complex m). VIII: δ 0.9–1.9 (m, 10), 5.53 (quintet, 2). IX and X: δ 1.5–2.3 (m, 7), 5.36 (d, 1), 5.74 (m, 2). XI: δ 1.18–2.30 (complex m, 7), 4.60 (d, 2), 5.69 (broad s, 2). XII: δ 1.22 (d, 3), 1.72 (d, 3), 2.03 (m, 1), 5.28 (s, 1), 5.42 (m, 2). XIII and XIV mixture: δ 5.3–5.6 (complex m, 3), 1.00–2.41 (complex m, 7). XV: δ 0.99–2.3 (m, 11), 5.50 (t, 1), 5.59 (m, 2). XVI: δ 0.95–2.22 (m, 14), 5.42 (broad s, 1), 5.53 (t, 1).

As can be seen from Table I, in some cases cyclic materials were obtained as byproducts in the hydrosilylation reaction. To test whether the alkenyldichlorosilanes were precursors to these cyclic products, samples of the dichlorosilyl adducts were treated with chloroplatinic acid. The results in Table II, examples 1, 2, 3, 7, and 12, indicate this was the case.

The cyclic structures were readily identified by the absence of Si–H and olefinic protons in the IR and NMR spectra. In all cases, high-boiling material was also formed, probably the result of intermolecular hydrosilylation reactions.

Previous cyclizations of alkenylsilanes have been performed on compounds containing terminal double bonds.[7,8] Therefore, only addition to the terminal position was required to produce the cyclic compounds. In the work reported here, one can see that in several cases intramolecular bond migration was a prerequisite to ring closure. This was not unexpected since alkyldichlorosilanes and chloroplatinic acid have been shown to cause isomerization of olefins.[9]

Generally, the cyclizations went well. The only compounds which failed to cyclize under our conditions were V and VI. This is likely only a rate factor since cyclization to five-membered rings in these two cases would require the isomerization of trialkylated olefins to terminal monoalkylated ones and hence may be rather slow.

As can be seen from Tables I and II, most of the cyclizations resulted in five-membered rings. Even in the cyclization of the pentenyldichlorosilanes (XII, XIII, and XIV), the silacyclopentane compound was formed preferentially (Table II, entry 2). This tendency to form five-membered rings when the cyclization is catalyzed by chloroplatinic acid has been demonstrated in other systems as well.[7,10]

In addition to the cyclic silicon compounds obtained, several novel bicyclic compounds were produced. In all cases, the procedures represent short, facile syntheses of these compounds, which would be difficult, if not impossible, to obtain by other methods. One such compound was obtained by treating the mixture of 3- and 4-dichlorosilylcyclohexenes with chloroplatinic acid, eq 4. The 7,7-dichloro-7-silanorbornane

Table II. Heterocyclic Organosilanes and Their Precursors[a]

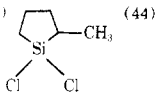
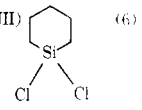
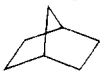
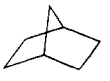
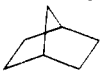
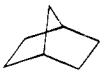
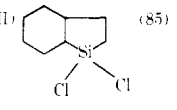
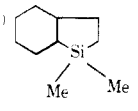
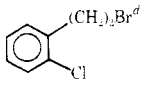
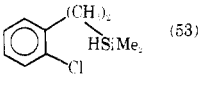
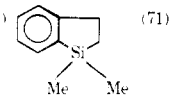
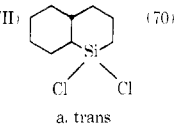
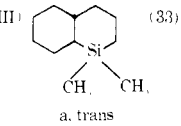
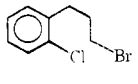
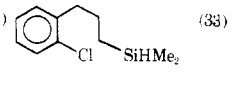
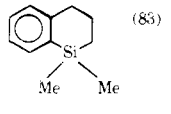
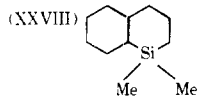
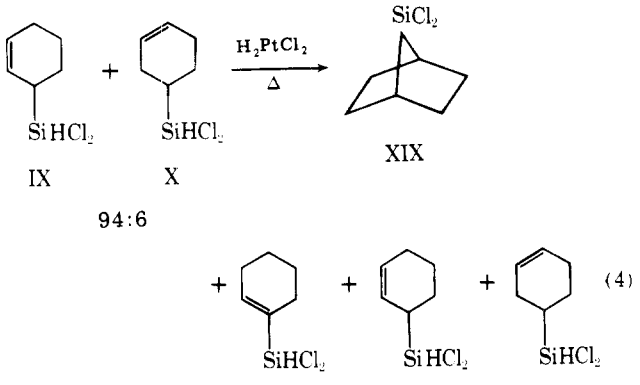
starting silane(s)	other reactants[b]	product(s) (% yield)	registry no.
(1) I, II, III	cat.	III (48)	
(2) XII, XIII, XIV	cat.	(XVII)  (44)	55909-49-4
		(XVIII)  (6)	2406-34-0
(3) IX	cat.	(XIX) $SiCl_2$ (55) 	69238-91-1
(4) XIX (crude)	MeLi	(XX) $Si(Me)_2$ (46) + 1-, 3-, 4-cyclohexenyltrimethylsilanes 	69238-92-2
(5) XIX	PhMgBr	(XXI) $Si(Ph)_2$ (65) 	69238-93-3
(6) XIX	$LiAlH_4$	(XXII) SiH_2 (40) 	328-56-3
(7) XV	cat.	(XXIII)  (85)	
		a, trans (20%)	69238-94-4
		b, cis (80%)	69238-95-5
(8) XXIIIa and -b	MeMgBr	(XXIV) 	
		a, trans (20%)	69238-96-6
		b, cis (80%)	69238-97-7
(9) 	(1) Mg; Et_2O (2) Me_2SiHCl	(XXV)  (53)	69238-98-8
(10) XXV	$PhCH_3$ + Na	(XXVI)  (71)	17158-48-4
(11) XXVI	H_2; Δ; Ni	(XXIV) a, trans (3%) (90) b, cis (97%)	
(12) XVI	cat.	(XXVII)  (70)	69238-99-9
		a, trans	
(13) XXVII	MeMgBr; Et_2O	(XXVIII)  (33)	69239-00-5
		a, trans	
(14) 	(1) Mg; Et_2O (2) $SiHCl_3$ (3) MeMgI	(XXIX)  (33)	17158-50-8
(15) XXIX	$PhCH_3$ + Na	(XXX)  (83)	17158-49-5

Table II (*Continued*)

starting silane(s)	other reactants[b]	product(s) (% yield)	registry no.
(16) XXX	H_2; Δ; Ni	(XXVIII)  (75) a, trans (20%) b, cis (80%)	69239-01-6

[a] Satisfactory analytical data (±0.3% for C, H, Si, Cl) were reported for all new compounds listed in this table. [b] Throughout this table, the abbreviation "cat." refers to the chloroplatinic acid–isopropyl alcohol catalyst solution described in the first part of the Experimental Section. [c] The NMR data which follow were obtained in a solution of CCl_4–Me_4Si in every case. Compound XIX: δ 1.2–2.3 (complex m). XX: δ 0.20 (s, 6 H), 1.02 (broad s, 2 H), and 1.25–2.18 (complex m, 8 H). XXI: δ 1.42–2.17 (complex m, 10 H), 7.11–7.70 (complex m, 10 H). XXII: δ 0.80–2.45 (complex m, 10 H), 3.59 (broad s, 2 H). XXIIIa: δ 0.50–2.42 (complex m). (XXIIIb): δ 1.0–2.2 (complex m). XXIVa: δ 0.0 (s, 3), 0.15 (s, 3), 0.5–2.1 (m, 14). XXIVb: δ 0.05 (s, 3), 0.15 (s, 3), 0.45–2.10 (m, 14). XXVI: δ 0.45 (s, 6), 1.2 (t, 2), 3.24 (t, 2), 7.22–7.64 (m, 4). XXVII: δ 0.57–2.22 (complex m). XXVIIIa: δ 0.05 (closely spaced d, 6), 0.32–2.0 (m, 16). XXIX: δ 0.12 (d, 6), 0.5–0.87 (m, 2), 1.47–2.0 (m, 2), 2.82 (t, 2), 3.95 (m, 1), 7.2 (m, 4). XXX: δ 0.33 (s, 6), 0.85–1.12 (m, 2), 1.85–2.27 (m, 2), 2.78–2.97 (m, 2), 7.0–7.58 (m, 4). [d] Registry no. 16793-91-2. [e] Registry no. 54877-27-9.



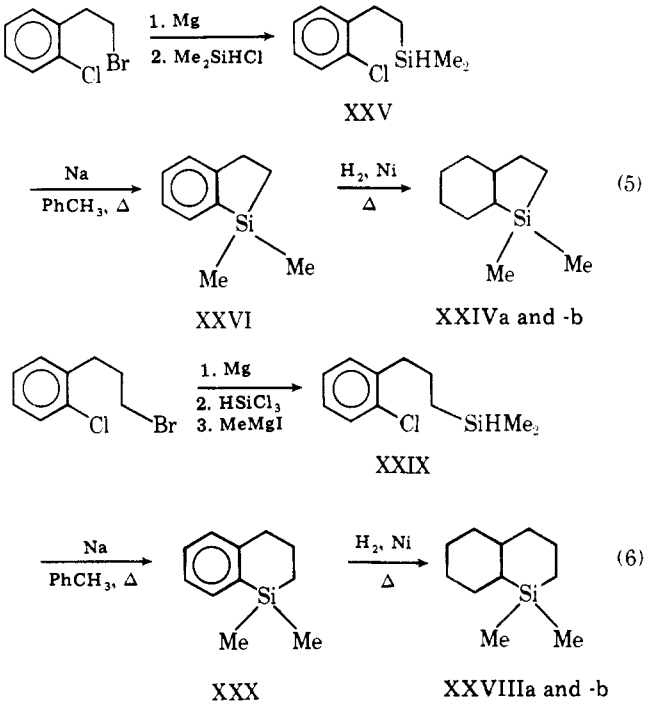
(4)

(XIX) was obtained along with 1-, 3- and 4-dichlorosilylcyclohexenes. The fact that the double bond had been scrambled was proved by methylation of the three latter compounds followed by comparison to authentic samples. As further structure proofs XIX was treated with both phenylmagnesium bromide and $LiAlH_4$ and the products were analyzed. All analytical methods (NMR, ^{13}C NMR, IR, and C, H analysis) pointed to this type of bicyclic structure.

Initial attempts to ring close the mixture of IX and X were complicated by rather erratic reaction times and poor yields. It was found that small amounts of the monochlorosilyl product XI caused an induction period and seemed to affect the activity of the catalyst. When this impurity[11] was removed by fractional distillation, the problem disappeared and the formation of XIX occurred normally. To prove this point, 4-cyclohexenylchlorosilane was added in varied amounts to the mixture of pure IX and X. It was found that in small amounts (~2%) the monochlorosilyl adduct had no effect on ring closure but at higher concentrations (~10%) caused an induction period and slowed the rate of cyclization. After all of the monochlorosilane reacts, the dichlorosilane can compete effectively for the catalyst and the cyclization proceeds normally.[12]

The ring closures of XV and XVI were effected giving novel [4.3.0] and [4.4.0] bicyclic compounds (XXIII and XXVII, respectively). The bicyclic frameworks were confirmed by comparison to authentic samples prepared in accord with the sequences in eq 5 and 6.

The ring closure of XVI in the presence of chloroplatinic acid produced only one stereoisomer, which was identified as having a trans ring juncture (Table II, entry 12). This was expected, since cis addition to the olefinic moiety should give the trans product.[2] This ring juncture was determined by methylating XXVII. The NMR spectrum of the methylated product was identical to that of XXVIIIa, eq 6, and also quite

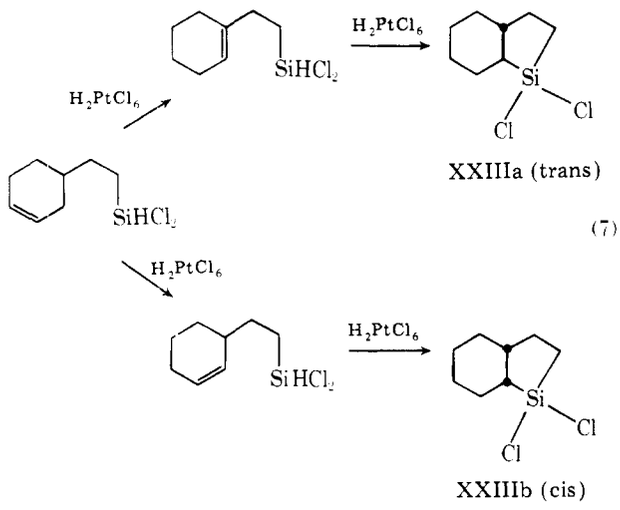


similar to the NMR of XXIVa to which the trans structure could be unequivocably assigned (vide infra). Likewise the NMR spectrum of XXVIIIb, eq 6, was very similar to that of XXIVb which had been assigned the cis structure.

Unlike XVI, ring closure of XV gave two isomers (cis and trans). The fact that both had the [4.3.0] framework was confirmed by comparison with authentic samples of the dimethyl derivatives. The stereochemical assignment of the isomers was determined by variable temperature NMR of the dimethyl derivatives. The major isomer from the ring closure (and hydrogenation) was examined at temperatures down to −90 °C in an XL-100 NMR spectrometer. As the temperature was lowered, one of the $\equiv SiCH_3$ groups broadened, while the other remained sharp. Since only the cis isomer can demonstrate conformational mobility, the major isomer was assigned that stereochemistry. As might be expected, the trans isomer did not show a similar effect when the temperature was lowered.

Obviously, bond migration is a prerequisite in the ring closure of XV. Because of the unequal isomer distribution obtained in the ring closure (80% cis, 20% trans), it seems unlikely that both isomers arise from the same transition state. If this is the case, then the trans isomer must come about when

the double bond is in the 1 position, while the cis isomer arises when it is in the 2 position, eq 7.



The fact that the side chain is rather short in the starting material (contains only two C atoms) might suggest that a trans isomer could form only slowly, if at all, when the double bond is in the 2 position. An examination of molecular models tends to substantiate this, but this explanation remains to be proven.

Experimental Section

Dichlorosilane (Union Carbide) and 1,3-butadiene (Matheson) were used as received. Analysis by VPC (10% SE -30, 45 °C) indicated that the dichlorosilane contained 3–5% of monochlorosilane as an impurity. Isoprene (Eastman), 4-vinylcyclohexene (Aldrich), 1,3-cyclohexadiene (Aldrich), and 1,4-cyclohexadiene (Columbia) were distilled before use. 1-Allylcyclohexene[13] was prepared by addition of allylmagnesium bromide to cyclohexanone followed by dehydration with *p*-toluenesulfonic acid.

The catalyst was a solution of chloroplatinic acid in isopropyl alcohol (0.05 g/mL). The solution was allowed to stand for a few weeks before use.[14] Routine VPC work was carried out on Varian Aerograph Model 202 and Model 920 gas chromatographs. Analyses by capillary VPC were conducted using a Perkin-Elmer Model 226 chromatograph. Infrared spectra were obtained from a Perkin-Elmer 137 spectrophotometer and NMR spectra were obtained from a Varian A-60, XL-100, or Perkin-Elmer R-32 spectrometer. Elemental analyses were performed by Dr. C. S. Yeh in the Microanalytical Laboratory of the Department of Chemistry, Purdue University.

Addition of Dichlorosilane to Dienes, General Procedure: The diene and catalyst were placed in a 150-mL stainless steel bomb (HOKE DOT-3E-1800) and cooled to −78 °C while flushing with N_2. Dichlorosilane was distilled under N_2 into a cold (−78 °C) calibrated tube. It was then distilled into the cold bomb which was sealed with a needle valve. The bomb was warmed to room temperature and then heated in hot oil for the appropriate time. The time and temperature of the reactions can be found in Table I. Upon cooling, excess dichlorosilane was vented and the contents removed with dry pentane. The pentane was removed and the resiude distilled.

Formation of Ring Closed Products. General Procedure: Into a dry, two-neck flask equipped with magnetic stirrer, nitrogen inlet, and septum was charged the appropriate silane(s) and catalyst solution. The mixture was heated, with stirring, and a positive pressure of N_2 was maintained. After the reaction was complete (determined by VPC), the contents were distilled and analyzed.

1,3-Butadiene. 1,3-Butadiene (8.7 mL, 5.4 g, 0.10 mol), dichlorosilane (14.2 mL, 0.2 mol), and 50 μL of catalyst solution were used in accord with the general procedure. Distillation of residue afforded two fractions: (1) 14.7 g bp 54–60 °C (60 mm) and (2) 1.5 g bp 57–63 °C (1 mm). VPC (SE 30, 100 °C) showed fraction (1) was composed of compounds I, II, and III. Analysis of fraction (2) (SE-30 column, 190 °C) showed only IV. See Table I.

Fraction (1) from above was treated with methyllithium in ether giving a 69% yield of methylated adducts: bp 54–58 °C (115 mm) (lit.[15] bp 110–115 °C). Analysis by capillary VPC showed it to contain equal amounts of *cis*- and *trans*-1-trimethylsilyl-2-butenes. These were identified by comparison of their NMR spectra with known samples.[16]

Isoprene. Isoprene (6.8 g, 10 mL, 0.1 mol), dichlorosilane (14.2 mL, 0.2 mol), and 50 μL of catalyst solution were used (see General Procedure). Distillation afforded two fractions: (1) 10.5 g bp 55–60 °C (25 mm) and (2) 0.4 g bp 73–76 °C (0.9 mm). VPC analysis (SE-30, 100 °C) showed fraction (1) containd V and VI in 59% yield which could not be separated and VII (4%). The mass spectrum for VII displayed molecular ions at *m/e* 168 and 170. Analysis of fraction (2) (SE-30, 200 °C) indicated the presence of VIII (65%, 10% yield) and several minor impurities. See Table I.

Methylation of the mixture of V and VI with ethereal methyllithium gave a 90% yield of a 50:50 mixture of 1-trimethylsilyl-2- and 3-methyl-2-butenes, bp 74–78 °C (100 mm). Hydrogenation of these two olefins at 1500 psi (Raney Ni) gave products identical in every way with authentic samples (see next paragraph) of 1-trimethylsilyl-2- and -3-methylbutanes (33 and 65%, respectively).

An authentic sample of 1-trimethylsilyl-2-methylbutane was prepared (57%) by coupling trimethylchlorosilane with 2-methylbutylmagnesium chloride in THF. It had identical physical properties with those described in the literature[17] and also with the material produced by hydrogenation of the adducts (see above). Similarly an authentic sample of 1-trimethylsilyl-3-methylbutane was prepared (63%) which proved identical in every respect to the hydrogenation product derived from the adduct above.

1,3-Cyclohexadiene. Dichlorosilane (21.3 mL, 0.3 mol), 1,3-cyclohexadiene (12.0 g, 0.15 mol), and 50 μL of catalyst solution were used. Distillation of the product afforded 11.1 g of only one fraction, bp 44–46 °C (4 mm). Analysis by VPC gave only one peak (41% yield) which later (see methylations below) proved to be a mixture of 3- (IX) and 4- (X) -cyclohexenyldichlorosilane (96 and 4%, respectively). These could not be readily separated. Other runs, under ostensibly the same conditions, gave rather erratic yields (30–60%) of the same mixture.

The mixture of IX and X obtained above was methylated in 85% yield by methyllithium in ether. Distillation yielded only one fraction, bp 65–67 °C (20 mm). Analysis by capillary VPC (Apiezon L-SF-96 in tandem, 120 °C) indicated two components, 3- and 4-trimethylsilycyclohexene, in a ratio of 96:4. Authentic samples of the two latter compounds were prepared. Equimolar quantities of trimethylchlorosilane and 3-cyclohexenylmagnesium bromide in THF produced 3-trimethylsilylcyclohexene: bp 53–55 °C (10 mm); n^{24}_D 1.4622 (lit.[18] n^{20}_D 1.4629). The 4-trimethylsilylcyclohexene was prepared in 83% yield from 4-trichlorosilylcyclohexene[19] and ethereal methylmagnesium bromide: bp 68–70 °C (21 mm), n^{20}_D 1.4601 (lit.[20] bp 175–176 °C; n^{20}_D 1.4600). These two authentic samples agreed in physical properties (IR, NMR) with the methylated samples obtained from IX and X. Likewise an authentic sample of 1-trimethylsilylcyclohexene was prepared by treating 1-cyclohexenyllithium (100 mL of a 0.51 M solution, 51 mmol) with chlorotrimethylsilane (8.15 g, 75 mmol) and refluxing for 14 h. Hydrolysis and normal workup afforded 6.1 g (78% yield) of product: bp 75–79 °C (20 mm); n^{20}_D 1.4630 (lit.[21] bp 77–79 °C (23 mm); n^{20}_D 1.4629).

1,4-Cyclohexadiene. Dichlorosilane (42 mL, 0.6 mol), 1,4-cyclohexadiene (40 g, 0.5 mol), and 250 μL of catalyst solution were used. Distillation of the product through a 91 cm, platinum spinning band distillation column (Perkin-Elmer) afforded a small forerun and a main fraction, 63.5 g, bp 75–77 °C (19 mm). VPC seemed to indicate this main fraction was composed of only one component (70% yield) which matched exactly the IR and NMR of adduct IX (3-cyclohexenyldichlorosilane) obtained from 1,3 cyclohexadiene. Analysis of the forerun by VPC and NMR indicated it was mostly a monochlorosilyl adduct, either 3- or 4-cyclohexenylchlorosilane (XI). In successive runs, the yield of the latter varied between 3 and 8%.

The dichlorosilyl adduct (main fraction) from the 1,4-cyclohexadiene was methylated in 90% yield by ethereal methyllithium. Analysis by capillary VPC indicated the product of this methylation contained two compounds, the 3- and 4-trimethylsilylcyclohexenes in a 94:6 ratio.

1,3-Pentadiene. Dichlorosilane (14.2 mL, 0.2 mol), 1,3-pentadiene (7.7 g, 0.1 mol), and 50 μL of catalyst solution were used. Distillation afforded two components: (1) 8.1 g bp 43–49 °C (15 mm) and (2) 0.8 g bp 70–75 °C (1 mm). VPC analysis (SE-30, 125 °C) of the first fraction showed the presence of *trans*-4-dichlorosilyl-2-pentene (XII) (15% yield) (strong trans band at 10.4 μm) and a mixture of 1-dichlorosilyl-2- and -3-pentenes (XIII and XIV) (33% yield). VPC analysis of fraction (2) above showed many components all overlapping. Because of the small amount of this fraction (0.8 g), no further work was done with it.

4-Vinylcyclohexene. Dichlorosilane (14.2 mL, 0.2 mol), 4-vinylcyclohexene (10.8 g, 0.1 mol), and 50 μL of catalyst solution were used. Distillation afforded one fraction (17.4 g), bp 54 °C (0.6 mm). VPC

analysis showed only one component, [2-(3-cyclohexenyl)ethyl]dichlorosilane (XV), 83% yield.

1-Allylcyclohexene.[13] Dichlorosilane (14.2 mL, 0.2 mol), 1-allylcyclohexene (12.2 g, 0.1 mol), and 50 μL of catalyst solution were used. Distillation afforded one fraction, 17.2 g, bp 61–64 °C (0.5 mm). VPC analysis (SE-30, 190 °C) indicated one major component, [3-(1-cyclohexenyl)propyl]dichlorosilane (XVI), (93% pure) 72% yield.

Structure Proofs and Ring Closures. 1,1-Dichloro-1-silacyclopentane (III). A mixture of I (27%), II (65%), and III (8%) (5.8 g, 0.034 mol) and 50 μL of catalyst solution was stirred for 2 h during which time an exothermic reaction occurred. Distillation afforded 3.0 g (48%) of compound III. The structure of III was confirmed by comparison of its IR and NMR with an authentic sample.[21]

1,1-Dichloro-2-methyl-1-silacyclopentane (XVII). A mixture of XII (33%), XIII, and XIV (67%) (3.2 g, 0.019 mol), and 50 μL of catalyst solution was stirred at 30–39 °C for 19 h. Distillation afforded 1.5 g of compound XVII (44% yield) and 1,1-dichloro-1-silacyclohexane[22] (XVIII) (6%). Compound XVII was identified by a comparison of its IR and NMR spectra with those of its isomer, compound VII. Compound XVIII was identified by matching its NMR spectrum with that of an authentic sample.[22]

7,7-Dichloro-7-silanorbornane (XIX). Compound IX (10.6 g, 0.06 mol) and 50 μL of catalyst solution were heated to 75 °C for 53 h. Distillation afforded 6.8 g of material, bp 34–35 °C (1.0 mm). VPC analysis (SE-30, 160 °C) indicated two components. The first was a mixture of 3- and 4-cyclohexenyldichlorosilane (2%). The second was a mixture of 1-cyclohexenyldichlorosilane (6%) and 7,7-dichloro-7-silanorbornane (XIX) (55% yield).

In other runs, ring closure required 12–160 h depending on the amount of compound IX used.

A large scale preparation of isomerically pure XIX was carried out as follows. Compound IX (45.4 g, 0.25 mol) and 250 μL of catalyst solution were allowed to react at 100 °C for 160 h. The crude mixture was divided roughly into two equal portions of 18.2 g each. To each portion was added 40 mL of CCl_4 and benzoyl peroxide (2.4 g, 0.01 mol). Each portion was refluxed for 10 h and the solvent removed. The portions were combined and distilled through a 91-cm platinum spinning band column, bp 75–78 °C (19 mm); yield of XIX was 27.0 g (60%). VPC and NMR indicated that all the isomeric cyclohexenyldichlorosilanes had been removed.

7,7-Dimethyl-7-silanorbornane (XX). A portion (7.7 g) of the undistilled mixture obtained from the ring closure of IX (see above) was treated with 0.25 mol of ethereal methyllithium at room temperature for 15 h. After normal workup and distillation, 3.7 g of material was obtained, bp 56 (10 mm) to 65 °C (30 mm). Analysis by capillary VPC indicated there were four components. The first three were tentatively identified by coinjection with authentic samples (vide infra) to be 1- (21%), 3- (4%), and 4- (1%) -cyclohexenyltrimethylsilanes (16% total yield). The fourth component was collected by preparative VPC (Se-30, 100 °C) and found to be 7,7-dimethyl-7-silanorbornane (XX) (46% yield).

7,7-Diphenyl-7-silanorbornane (XXI). Compound XIX, 4.5 g (0.025 mol), was refluxed for 5 days in THF with phenylmagnesium bromide (0.1 mol). After normal workup and solvent removal, the crude product was taken up in hexane. Cooling afforded a crude crystalline product. After two crystallizations from hexane, 4.3 g of XXI was obtained (65%) melting at 107–111 °C. An additional five crystallizations from hexane raised the mp to 111–112.5 °C.

7-Silanorbornane (XXII). Compound XIX (45.2 g, 0.25 mol) was treated with $LiAlH_4$ (14.2 g, 0.375 mol) in ether. Hydrolysis and normal workup were followed by sublimation (room temperature, 20 mm) which afforded 11.1 g (40%) of 97% pure XXII. An analytical sample (preparative VPC) melted at 67–68 °C. A ^{13}C-NMR spectrum indicated only two different carbon atoms in a ratio of 4:2 and mass spectral analysis gave a molecular ion at *m/e* 112.

4-Chlorosilylcyclohexene (XI). 4-Cyclohexenylsilane [obtained from $LiAlH_4$ reduction of 4-cyclohexenyltrichlorosilane (63% yield)], 2.4 g (21 mmol), was dissolved in 25 mL of dry ether. Anhydrous stannic chloride[23] (6.0 g, 2.7 mL, 23 mmol) was added dropwise causing an exothermic reaction and the immediate preciptation of stannous chloride. The mixture was refluxed for 5 h and then poured into 50 mL of dry pentane. Filtration, solvent removal, and distillation afforded 2.0 g (65% yield) of XI, bp 75–78 °C (51 mm).

Deleterious Effect of 4-Cyclohexenylchlorosilane (XI) on Ring Closure. Into each of three flasks was placed 3.62 g (20 mmol) of IX along with 0, 2, and 10 mol % of XI, respectively. Catalyst solution (20 μL) was added to each and all three were then heated to 70 °C. The mixture containing the 10 mol % of XI displayed an induction period and the ring closed to XIX slower than the others. In the latter two cases, ring closure was complete in 12 h, but the one containing 10 mol % of XI required 24 h for completion.

7,7-Dichloro-7-silabicyclo[4.3.0.]nonane (XXIII). Compound XV (15.6 g, 0.075 mol) and 50 μL of catalyst solution were heated at 100 °C for 8 h. Distillation afforded 13.2 g (85% yield) of compound XXIII consisting of an isomer mixture composed of 20% trans (XXIIIa) and 80% cis (XXIIIb), bp 51–54 °C (0.2 mm). Analytical samples were obtained from preparative VPC (SE-30, 200 °C).

An isomeric mixture (20% trans and 80% cis) of compound XXIII (11.6 g, 0.05 mol) was refluxed with 0.15 mol of methylmagnesium bromide for 12 h. Normal workup and solvent removal afforded (5.6 g, 60% yield) 20% *trans*- and 80% *cis*-XXIV.

[2-(*o*-Chlorophenyl)ethyl]dimethylsilane (XXV) was prepared in 53% yield in essential accord with literature[24] directions from 19.7 g (0.09 mol) of 2-(*o*-chlorophenyl)ethyl bromide[25] and chlorodimethylsilane, bp of product 93–95 °C (4.7 mm).

2,3-Benzo-1,1-dimethyl-1-silacyclopent-2-ene (XXVI). Compound XXV (17.9 g, 0.09 mol) was cyclized according to literature[24,25] directions, affording 10.4 g (71%) of compound XXVI, bp 80–88 °C (14 mm).

Authentic 7,7-Dimethyl-7-silabicyclo[4.3.0.]nonane. Compound XXVI (5.6 g) was hydrogenated at 1500 psi (100 °C, 5 h) using 1.5 g of W-2 Raney nickel in 30 μL of methylcyclohexane. Distillation afforded 5.3 g (90%) of compound XXIV, bp 117–122 °C (104 mm), with a trans to cis ratio of 3/97. Analytical samples were obtained by VPC (SE-30, 200 °C) and these compared exactly (IR) to compounds XXIVa and XXIVb prepared by the ring closure of XV followed by methylation (vide supra).

NMR Study of Compounds XXIVa and XXIVb. A sample of XXIVa (trans) was dissolved in CH_2Cl_2 and the NMR spectra of the $SiCH_3$ protons recorded at various tempertures down to −90 °C. No broadening of the peaks was observed. Similarly, a sample of the cis isomer (XXIVb) was studied in the XL-100 spectrometer. At −60 °C a broadening of one of the silicon methyl ($SiCH_3$) peaks was observed. Further broadening was noted down to −90 °C when it seemed that the peak actually consisted of two broad peaks coalescing together. This indicated that isomer XXIVb had conformational mobility suggesting strongly that it was the cis isomer.

***trans*-2,2-Dichloro-2-silabicyclo[4.4.0.]decane (XXVII).** Compound XVI (10.6 g, 93% pure, 0.004 mol) and 50 μL of catalyst solution were heated at 132–135 °C for 12 h and at 140 °C for 4 h. Distillation gave 7.2 g (95% pure, 70% yield) of compound XXVII, bp 62–63 °C (0.4 mm). The mass spectrum gave molecular ions, *m/e* at 222 (100) and 224 (68).

Compound XXVII was methylated in 33% yield by treatment with ethereal methylmagnesium bromide at room temperature for 26 h. The methylated derivative (XXVIIIa) boiled at 60 °C (2 mm).

[3-(*o*-Chlorophenyl)propyl]dimethylsilane (XXIX). Pure 1-chloro-2(3-bromopropyl)benzene[24] (142 g, 0.61 mol) was converted to its Grignard reagent by treatment with 36 g (1.5 g-atom) of Mg in 0.7 L of ether. This solution was added to $SiHCl_3$ (200 mL, 0.2 mol) at 0 °C. After 1 h at room temperature, the salts were filtered and the solvent removed. The crude product was methylated immediately with 1.7 mol of CH_3MgI at room temperature for 18 h. Normal workup and distillation afforded 43.2 g (33% yield) of compound XXIX, bp 93–95 °C (2.8 mm).

2,3-Benzo-1,1-dimethyl-1-silacyclohex-2-ene (XXX). Compound XXIX (42.0 g, 0.197 mol) was cyclized in accord with analogous literature[24,25] directions affording 29.0 g (83% yield) of product boiling at 78–79 °C (3.6 mm). Its mass spectrum showed a molecular ion, *m/e* 176.

Authentic 2,2-Dimethyl-2-silabicyclo[4.4.0.]decane (XXVIII). Compound XXX was hydrogenated at 1500 psi (70–150 °C, 2 h) with W-2 Raney nickel in 30 mL of methylcyclohexane. Distillation afforded 9.4 g (75% yield), bp 71–73 °C (2.9 mm), of 20% XXVIIIa (trans) and 80% XXVIIIb (cis). In analyzing this mixture by VPC (SE-30, 170 °C, FFAP, 140 °C), the trans isomer eluted first as expected. Analytical samples were obtained from preparative VPC. The trans isomer corresponded exactly (NMR, IR) to the product XXVIIIa obtained from the ring closure of XVI followed by methylation.

Acknowledgment. We wish to thank the Dow Corning Corporation whose financial assistance made this work possible.

Registry No.—Dichlorosilane, 4109-96-0; chloroplatinic acid, 16941-12-1; 1-trimethylsilyl-2-methyl-2-butene, 18293-98-6; 1-trimethylsilyl-3-methyl-2-butene, 18293-99-7; 1-trimethylsilyl-2-methylbutane, 18291-14-0; 1-trimethylsilyl-3-methylbutane, 18291-15-1; trimethylchlorosilane, 75-77-4; 2-methylbutylmagnesium

chloride, 32115-62-1; 3-trimethylsilylcyclohexene, 40934-71-2; 4-trimethylsilylcyclohexene, 40934-72-3; 3-cyclohexenylmagnesium bromide, 31463-48-6; 4-trichlorosilylcyclohexene, 10137-69-6; methylmagnesium bromide, 75-16-1; 1-trimethylsilylcyclohexene, 17874-17-8; 1-cyclohexenyllithium, 37609-34-0; 1-cyclohexenyldichlorosilane, 69239-02-7; phenylmagnesium bromide, 100-58-3; 4-cyclohexenylsilane, 69239-03-8; chlorodimethylsilane, 1066-35-9; trichlorosilane, 10025-78-2.

References and Notes

(1) R. A. Benkeser and W. C. Muench, *J. Am. Chem. Soc.*, **95**, 285 (1973).
(2) R. A. Benkeser and D. F. Ehler, *J. Organomet. Chem.*, **69**, 193 (1974).
(3) R. A. Benkeser, F. M. Merritt II, and R. T. Roche, *J. Organomet. Chem.*, **156**, 235 (1978).
(4) K. Yamamoto and M. Kumada, *J. Organomet. Chem.*, **13**, 131 (1968).
(5) W. C. Muench, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1973.
(6) E. C. Mozdzen, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1978.
(7) H. Sakurai, T. Hirose, and A. Hosomi, *J. Organomet. Chem.*, **86**, 197 (1975).
(8) J. V. Swisher and H. H. Chen, *J. Organomet. Chem.*, **69**, 83 (1974).
(9) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).
(10) R. J. Fessenden and W. D. Kray, *J. Org. Chem.*, **38**, 87 (1973).
(11) A small amount of H_3SiCl is present in the H_2SiCl_2 but likely more is generated by some disproportionation of the latter.
(12) Plenary Main Section, *Lect. Int. Congr. Pure Appl. Chem. 24th*, **4**, 31 (1974).
(13) J. J. Eisch and G. R. Husk, *J. Org. Chem.*, **31**, 3419 (1966).
(14) Changes in catalytic activity seemed to occur when fresh solutions were used.
(15) D. Seyferth, T. F. Jula, H. Dertouzos, and M. Pereyre, *J. Organomet. Chem.*, **11**, 63 (1968).
(16) D. A. Jones, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1968.
(17) J. C. Saam and J. L. Speier, *J. Am. Chem. Soc.*, **83**, 1351 (1961).
(18) Y. Kiso, K. Yamamoto, K. Tamao, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 4373 (1972).
(19) G. H. Wagner, D. L. Bailey, A. N. Pines, M. L. Dunham, and D. B. McIntire, *Ind. Eng. Chem.*, **45**, 367 (1953).
(20) Y. Kiso, M. Kumada, K. Tamao, and M. Umeno, *J. Organomet. Chem.*, **50**, 297 (1973); K. R. Beck, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1970.
(21) Everett W. Bennett, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1958.
(22) R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).
(23) N. S. Nametkin and T. I. Chernysheva, *Dokl. Akad. Nauk. SSSR*, **178**, 165 (1968).
(24) H. Gilman and O. L. Marrs, *Chem. Ind. (London)*, 208 (1961).
(25) H. Gilman and O. L. Marrs, *J. Org. Chem.*, **29**, 3175 (1964).

Regio- and Stereochemistry of the Cycloadditions of Dichloroketene to 2-Methyl- and 3-Methyl-2-cholestene[1]

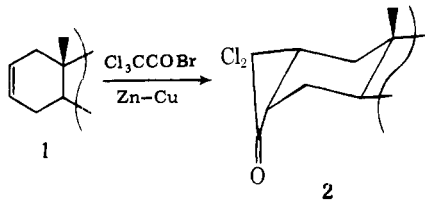
Alfred Hassner* and Larry R. Krepski

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901

Received June 8, 1978

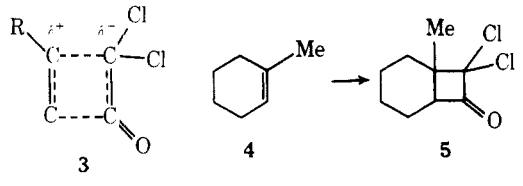
Electronic and stereoelectronic factors governing the cycloaddition of 2-methyl- and 3-methyl-2-cholestene (7 and 8) with dichloroketene were examined. In each case, the reaction was regio- and stereospecific: 2-methyl-2-cholestene (7) afforded 2a,2a-dichloro-2α,3α-ethano-2β-methylcholestan-3a-one (9), while 3-methyl-2-cholestene (8) afforded 3a,3a-dichloro-2α,3α-ethano-3β-methylcholestan-2a-one (13). The results indicate that the cycloaddition proceeds exclusively via attack of the ketene from the α side of the steroid and that the regiochemistry is guided largely by electronic factors. The structures of the cycloadducts were elucidated by chemical means (reduction, Baeyer–Villiger oxidation) and NMR, while circular dichroism proved useful in the conformational analysis of the fused steroidal cyclobutanones and lactones.

The formation of cyclobutanones by addition of dichloroketene[2] to reactive olefins has been the subject of many synthetic and mechanistic studies.[3,4] In cyclohexene systems the cycloaddition has been demonstrated to be highly regioselective[4,5] and occurs for stereoelectronic reasons with preferential axial bond formation between the carbonyl carbon and the cyclohexane chair conformation. Thus, generation of dichloroketene in the presence of 2-cholestene (1) was found[4] to yield almost exclusively **2**.



1 2

On the other hand, olefin substituents exert strong electronic effects that guide the regiochemistry of the cycloaddition. If a substituent R is capable of stabilizing a positive charge, then the reaction can be visualized to proceed via a transition state such as **3**. For instance, 1-methylcyclohexene (**4**) leads to cycloadduct **5**.[9]

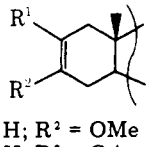


3 4 5

In light of the striking regioselectivity found[4b] in the 2-cholestene–dichloroketene reaction, we were interested in the effect an additional double-bond substituent would have on the regio- and stereochemistry of a dichloroketene cycloaddition. Until recently, the yield of cyclobutanones from the cycloaddition of dichloroketene to tri- and tetrasubstituted olefins has been low or nil.[2b,c] However, we have recently described[6] an improved procedure, using $POCl_3$, which overcomes these old difficulties. With this new method in hand, it was feasible to study the cyloaddition of dichloroketene to trisubstituted steroidal olefins.

Results and Discussion

The steroidal enol derivatives **6a–e** were studied in the re-



6a, R^1 = H; R^2 = OMe
b, R^1 = H; R^2 = OAc
c, R^1 = H; R^2 = $OSiMe_3$
d, R^1 = OAc; R^2 = H
e, R^1 = $OSi(Me_3)$-*t*-Bu; R^2 = H

0022-3263/79/1944-1376$01.00/0