

ORGANOSILICON COMPOUNDS. LXXXV.*

THE ADDITION OF DICHLOROCARBENE TO VINYLMETHYL-
CHLOROSILANES AND ALLYLMETHYLCHLOROSILANES

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The addition of the dichlorocarbene generated by pyrolysis of trichloromethyltrichlorosilane was used to prepare dichlorocyclopropane derivatives of methylchloro-substituted olefins. The approximate relative rate constants of the addition of dichlorocarbene to these olefins were determined by the method of competition reactions. Thermal stability of the formed cyclopropane derivatives in pure state and in the presence of the chlorosilanes formed in the reaction mixture was studied.

The study of the effect of chloro substituents attached to silicon on the character of the bond of silicon to vinyl group has so far been based on measurements of dipole moments of vinylmethylchlorosilanes¹, their infrared² and NMR spectra³. None of these studies has been devoted, however, to determination of the reactivity of these compounds in addition reactions of electrophilic reagents, although relative rates of the addition of dichlorocarbene turned out to be useful criterion for evaluating the effect of silyl groups in methylsilylolefins⁵, methyl(trimethylsilyloxy)silyl-substituted olefins⁴, bis(trimethylsilyl)olefins⁵, and methyl(tert-butoxy)silyl-substituted olefins⁶.

For this reason in the present work a study of the addition of electrophilic reagents to vinylmethylchlorosilanes and allylmethylchlorosilanes was undertaken. Based on the so far reported results in the allyl derivatives only the +I effect of silicon and the -I effect of chlorine atoms are operating. Therefore, from comparison of both series of these compounds some conclusions on the ($p \rightarrow d$) π character of the bond of silicon with vinyl group can be drawn^{4,5}. Due to the high reactivity of the silicon-chlorine bond in the studied models, of electrophilic reagents we have chosen only halogens and dihalocarbenes. As in the addition of chlorine concurrent radical course of the reaction can not be completely excluded, as well as the splitting of the silicon-carbon bond in allylchlorosilanes by the action of bromine, for both series of the compounds we used dichlorocarbene, and in the case of vinylmethylchlorosilanes also bromine, as electrophilic reagents. In this study dichlorocarbene was generated by pyrolysis of trichloromethyltrichlorosilane⁷.

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EXPERIMENTAL

Compounds and methods. Trichloromethyltrichlorosilane was prepared by UV light-induced chlorination of methyltrichlorosilane⁸ and was purified by distillation (b.p. 155°C, 65% yield). 1-Heptene was prepared by pyrolysis of heptyl acetate at 500°C⁹. Vinyltrichlorosilane (VÚOS Pardubice-Rybitví) and vinylmethylchlorosilane (from laboratory stock) were rectified prior to use. Vinylmethylchlorosilane was prepared by the vinylation of dimethylchlorosilane with vinylmagnesium chloride¹⁰. Vinyltrimethylsilane was prepared by the methylation of vinyltrichlorosilane with methylmagnesium chloride¹¹. Allylchlorosilane was obtained both by dehydrochlorination of γ -chloropropyltrichlorosilane¹⁰ and by a reaction of allylmagnesium bromide with silicon tetrachloride¹². Allylmethylchlorosilane and allyldimethylchlorosilane were prepared by a reaction of allylmagnesium bromide with methyltrichlorosilane and dimethyl-

TABLE I
Physical Constants of the Olefins

Olefin	B.p., °C found lit. (Torr)	n_D^{20} found lit.	d_4^{20} found lit.
1-Heptene	93.0	1.4002	0.6948
	93.643 ²⁵	1.39980 ²⁵	0.69698 ²⁵
1-Decene	169.5	1.4217	0.7395
	170.670 ²⁵	1.42146 ²⁵	0.74082 ²⁵
Cyclohexene	82.5	1.4540	0.8467
	83.0 ²⁵	1.44507 ^{a,25}	0.8102 ²⁵
Vinyltrichlorosilane	91.0	1.4241	1.2490
	92.5 (750) ²⁶	1.4295 ²⁶	1.2426 ²⁶
Vinylmethylchlorosilane	92.0	1.4293	1.0816
	91.0 (742) ²⁷	1.4270 ²⁷	1.0868 ²⁷
Vinylmethylchlorosilane	82.5	1.4162	0.8828
	82.0—82.5 ²⁸	1.4141 ^{b,28}	0.8744 ^{c,28}
Vinyltrimethylsilane	57.0	1.3904	0.6861
	54.4 (745.5) ¹¹	1.3910 ²⁹	0.6903 ²⁹
Allylchlorosilane	115.0	1.4450	1.232
	114.0—115.0 (743) ³⁰	1.4460 ³⁰	1.2011 ³⁰
Allylmethylchlorosilane	120.0	1.4407	1.066
	119.0—120.0 ³¹	1.4419 ³²	1.0758 ³³
Allyldimethylchlorosilane	110.0	1.4287	0.9008
	110.0 (733) ³⁴	1.4295 ³⁴	0.8964 ³⁴
Allylchlorosilane	84.5	1.4131	0.7150
	84.9 (737) ³⁵	1.4074 ³⁵	0.7193 ³⁵

^a n_D^{22} , ^b n_D^{25} , ^c d_{25}^{25} .

dichlorosilane, respectively¹³. Allyltrimethylsilane was obtained by the methylation of allyl-trichlorosilane with methylmagnesium chloride¹⁴. All the olefins were distilled on a 25 T π column filled with Dixon rings made from copper gauze; physical constants see Table I. 2,2-Dichloro-1-trichlorosilylcyclopropane was prepared by a reaction of 8.1 g (0.05 mol) of vinyltrichlorosilane with dichlorocarbene formed by pyrolysis of 12.5 g (0.05 mol) of trichloromethyltrichlorosilane (250°C, 30 min) in a 100 ml autoclave. The reaction mixture was freed from high boiling impurities by distillation from glass wool under vacuum of 10–20 Torr and 2,2-dichloro-1-trichlorosilylcyclopropane was isolated by preparative gas chromatography. Other silyl-substituted dichlorocyclopropanes were prepared similarly; physical properties see Table II. α,β -Dibromoethyltrichlorosilane was prepared by bromination of 81 g (0.5 mol) of vinyltrichlorosilane at 50°C

TABLE II

Physical Constants of Dichlorocyclopropane Derivatives of the Type $R^1CH-CHR^2$

R ¹	R ²	B.p., °C (Torr) found ^a lit.	n _D ²⁰ found lit.	d ²⁰ found lit.	Calculated/Found	
					% C	% H
—(CH ₂) ₄ —		152	1.5022	1.1230	43.49	6.03
		79.0–80.0 (15) ⁷				
CH ₃ (CH ₂) ₄ —	H	179	1.4495	1.0102	53.40	7.70
		199 ³⁶	1.4514 ⁵			
		67.0–69.0 (10) ⁵		1.029 ⁵	53.00	7.80
Cl ₃ Si—	H	193	1.4905	1.5165	15.08	1.22
			—	—	14.76	1.23
CH ₃ Cl ₂ Si—	H	192	1.4843	1.3361	21.20	2.66
			—	—	21.45	2.70
(CH ₃) ₂ ClSi—	H	183	1.4726	1.2072	29.18	3.94
			—	—	29.49	4.45
(CH ₃) ₃ Si—	H	168	1.4505	1.072	42.51	7.10
		166 ³⁶	1.4554 ⁵	1.052 ⁵	52.62	7.20
		89.0–90.0 (72) ⁵				
Cl ₃ SiCH ₂ —	H	213	1.4892	1.5061	13.62	1.70
			—	—	13.94	1.95
CH ₃ Cl ₂ SiCH ₂ —	H	211	1.4865	1.3412	25.02	3.15
			—	—	25.23	3.39
(CH ₃) ₂ ClSiCH ₂ —	H	206	1.4745	1.2167	32.70	5.27
			—	—	33.12	5.09
(CH ₃) ₃ SiCH ₂ —	H	194	1.4598	1.030	45.71	7.70
		187 ³⁶	1.4558 ⁵	1.022 ⁵	45.54	7.62
		79.0–80.0 (23) ⁵				

^a Determined from retention data.

TABLE III

Composition of Some Reaction Mixtures from the Preparation of Silyl-Substituted Dichlorocyclopropanes of the Type



R	Starting olefin	Trichloromethyltrichlorosilane	Silyl-substituted cyclopropane	Silicon tetrachloride	By-products ^a
(CH ₃) ₂ ClSi—	27.6	11.9	23.8	32.8	5.8 ^d
(CH ₃) ₃ Si—	29.4 ^b	—	40.5 ^c	—	30.0 ^e
(CH ₃) ₂ ClSiCH ₂ —	19.0	4.4	40.5	30.1	6.0 ^f
(CH ₃) ₃ SiCH ₂ —	8.1	2.7	41.4	27.7	20.3 ^g

^a Retention times and b.p. determined on their basis are given in Table IV. ^b A mixture of the unreacted olefin and silicon tetrachloride (not separable by g.l.c.). ^c A mixture of the cyclopropane and the unreacted trichloromethyltrichlorosilane (not separable by g.l.c.). ^d Compounds B and C (Table V) in the weight ratio 1 : 1.17. ^e Compounds A, B and C (Table V) in the weight ratio 4.48 : 1 : 1.5. ^f Compound B (Table V). ^g Compounds A and C (Table V) in the weight ratio 3.02 : 1.

TABLE IV

Retention Times^a and Boiling Points of By-Products in the Preparation of Silyl-Substituted Dichlorocyclopropanes

B.p. were determined from retention times.

Compound	Rel. retention time	B.p., °C
Allyl chloride	1.00	45 ²⁵
Silicon tetrachloride	1.4	56.7 ²⁵
Trimethylchlorosilane	1.5	57.7
Vinyltrimethylsilane	1.5	54.4 ¹¹
A	1.5	57
Tetrahydrofuran	2.4	64—65 ¹¹
C	2.5	65
Dimethyldichlorosilane	2.7	70.0
B	2.7	70
Benzene	3.3	80.1 ¹⁴
n-Heptane	5.7	98.4 ¹⁴

Relative retention times with respect to allyl chloride; stationary phase was 5% Silicone elastomer E 301 on grinded unglazed tiles.

for 2 h¹⁷; a distillation of the reaction mixture through a 7 TP column afforded 144 g (90%) of the product, b.p. 90°C/10 Torr, n_D^{20} 1.5367, d_4^{20} 2.044 (lit.¹⁷ gives b.p. 91°C/11 Torr, n_D^{20} 1.5370, d_4^{21} 2.05). 1,2-Dibromodecane was prepared similarly; b.p. 142.5°C/10 Torr, n_D^{20} 1.4918, d_4^{20} 1.363 (Lit.¹⁶ gives b.p. 145°C/15 Torr, d_4^{20} 1.3841, d_4^{30} 1.3512).

Determination of by-products. In Tables III and IV are presented the results of chromatographic analyses of the reaction mixtures from the preparation of some silyldichlorocyclopropanes. By comparison of retention times of by-products with those of standards on several stationary phases (silicon elastomer E 301, poly(ethylene glycol adipate), perfluoropropylsiloxane FS 16) substance A from Table IV was identified as trimethylchlorosilane and substance B was found to be dimethyldichlorosilane.

Preparatory measurements of relative rates of the addition of dichlorocarbenes. To a mixture of 1.2 g (7.5 mmol) of vinyltrichlorosilane and 0.7 g (7.1 mmol) of 1-heptene placed in a 20 ml glass ampoule were added 50 mg (0.2 mmol) of trichloromethyltrichlorosilane dissolved in 1 ml of tetrachloromethane. Sealed ampoule was heated in a metal bath to 250°C for 20 min; after cooling to room temperature the reaction mixture was analysed. With the other couples the reaction was carried out in a similar way. The molar volume of a measured olefin to the reference compound was reverse to the ratio of their reactivities which was determined by preliminary experiments. With the allylmethylchlorosilanes this ratio varied within the range 2 : 1 to 1 : 2, with the vinyl methylchlorosilanes it changed from 10 : 1 to 15 : 1. The reaction was carried out in *n*-heptane, *p*-xylene and in dibutyl ether.

Preparatory measurements of relative rates of the addition of bromine. To a mixture of 1.2 g (7.5 mmol) of vinyltrichlorosilane, 50 ml (0.4 mmol) of 1-decene and 0.75 ml of tetrachloromethane placed in a 5 ml-volumetric flask maintained at temperature 50°C were added 30 mg (0.1 mmol) of bromine. After discolouration the reaction mixture was analysed.

Analysis of reaction mixtures. Reaction mixtures were analysed on a gas chromatograph equipped with catharometer (Vývojové dílny ČSAV, Prague); the column was 310 cm long and filled with 5% silicone elastomer E 301 on grinded unglazed tiles (Spolana, Neratovice). The reaction mixtures from the couple vinyltrimethylsilane-1-heptene were analysed on a column 170 cm long (5% dinonyl phthalate (Lachema, Brno) on grinded unglazed tiles).

Testing of thermal stability of silyl-substituted dichlorocyclopropanes. 230 mg (0.26 mmol) of 2,2-dichloro-1-trimethylsilylcyclopropane were heated in sealed glass ampoule at 200°C for 1 h; after cooling in air the reaction mixture was analysed by gas chromatography. The other dichlorocyclopropanes were tested similarly.

Testing of thermal stability of silyl-substituted dichlorocyclopropanes in the presence of silicon tetrachloride. 336 mg (1.82 mmol) of 2,2-dichloro-1-trimethylsilylcyclopropane and 284 mg (1.67 mmol) of tetrachlorosilane were heated in sealed glass ampoule at 200°C for 1 h. After cooling in air the reaction mixture was analysed by gas chromatography (Table V).

The relative rate constants were calculated according to the formula $k_{rel} = k/k_0 = PN_0/P_0N$, where N is the mole fraction of a measured olefin, N_0 the molar fraction of a reference olefin, P , P_0 the mole fraction of the measured and the reference cyclopropane, respectively. The measurement of each relative rate constant was repeated from two to five times, and from the so obtained relative rate constants the average value, k_{rel} , was calculated. The difference between individual experimental rate constants and their average value, which was expressed in per cent of the experimental value, was taken as the relative error of the measurement, δ ; it changed within 0.8 to 13.0%. Maximum errors, δ_{max} , calculated for individual measurements are given in the table of corresponding relative rate constants.

TABLE V

Thermal Stability of Silyl-substituted Dichlorocyclopropanes of the Type R—CH—CH₂ on Heating to 200°C for 1 h

R	Composition of reaction mixture (w.%)			
	recovered cyclopropane	A	B	C
(CH ₃) ₂ ClSi—	89.8	—	8.2	1.2
	75.0 ^a	—	11.5 ^a	13.4 ^a
(CH ₃) ₃ Si—	91.9	6.6	—	1.5
	66.5 ^a	21.5 ^a	4.8 ^a	7.2 ^a
(CH ₃) ₂ ClSiCH ₂ —	90.5	—	9.5	—
	87.8 ^a	—	12.2	—
(CH ₃) ₃ SiCl ₂ —	86.8	11.1	—	2.1
	77.0 ^a	17.2 ^a	—	5.7 ^a

^a In the presence of silicon tetrachloride.

RESULTS AND DISCUSSION

The addition of bromine to vinylmethylchlorosilanes. The experiments carried out with the couple vinyltrichlorosilane-1-decene demonstrated an extraordinary high change of the values of relative rates of the addition of bromine with temperature within the temperature range +50 to -50°C at the molar ratio of vinyltrichlorosilane to 1-decene 15 : 1 in tetrachloromethane as solvent (k_{rel} at 50°C was 0.125, at 25°C it was 0.055, and at 0°C it equaled to 0.023). The time needed for complete disappearance of bromine was very long: at temperatures 50, 25 and 0°C it amounted to 1.5–3 h, at -25 and -50°C the reaction mixture was not discoloured even after 48 h. On the other hand, in preparatory measurements of relative rates of the bromination of vinyltrimethylsilane relative to 1-decene, and of 1-decene relative to 1-heptene, carried out in tetrachloromethane, at approximately the same molar ratio of bromine to 1-decene (1 : 1.5) the discolouration of the reaction mixture was completed after the period of 3–5 min. It seems likely that vinylchlorosilanes form a complex with bromine, which is the proper brominating agent whose reactivity is, however, substantially lower than that of bromine itself. If this is the case then it can be expected that the nature of the complex, and thus also its reactivity, will change with the number of chlorine atoms in the molecule of chlorosilanes; of course, in such a case the relative reactivity of chloro-substituted silylolefins cannot be estimated by the method described above. The additions of dichlorocarbene to silylolefins were studied in three different solvents; *p*-xylene, dibutyl ether, and *n*-heptane, because we have found that solvents strongly affect the selectivity of the so generated dichlorocarbene.

Evidence for the electrophilic character of pyrolytically generated dichlorocarbene. Unlike the dichlorocarbene generated by alkaline hydrolysis of chloroform^{17,18}, the electrophilic character of the dichlorocarbene formed by pyrolysis of trichloromethyltrichlorosilane⁷ has not yet been evidenced. We have therefore compared relative rates of the addition of the pyrolytically generated dichlorocarbene to cyclohexene, 1-heptene, and vinyltrimethylsilane with the rates of the addition of the dichlorocarbene generated by Doering-Hoffmann method¹⁷ and with those of the addition of bromine. In all three cases the reactivity sequence was the same — the rate of the addition decreased in the series cyclohexene, 1-heptene, vinyltrimethylsilane (Table VI).

The effect of reaction temperature on the selectivity of the addition of dichlorocarbene. The importance of this factor was checked with the couple vinyltrichlorosilane-cyclohexene at temperatures 150–270°C in tetrachloromethane as solvent. At temperatures 150 and 180°C the pyrolysis of trichloromethyltrichlorosilane does not proceed even after 24 h. Minimum decomposition temperature is thus 200°C. On the other hand, the temperature 275°C is too high, not only due to low selectivity of the reaction at this temperature, but also due to partial carbonisation of the reaction mixture and thus lower reproducibility of the results, which is demonstrated by much greater experimental error (8.99%). The dependence of relative rate constants of the addition on temperature is represented in Fig. 1.

Determination of approximate relative rates of the addition of dichlorocarbene. As it was found by preliminary experiments the selectivity of the addition of the dichlorocarbene generated by pyrolysis of trichloromethyltrichlorosilane is greatest at 200°C in dibutyl ether as solvent. Using these conditions we have determined relative rates of the addition to vinyl- and allylmethylchlorosilanes. With the couple vinyltrimethylsilane-1-heptene the measurements were carried out in dipropyl ether, since the retention time of dibutyl ether was very close to that of 2,2-dichloro-1-tri-

TABLE VI
Rate Constants k_{rel} of the Addition of Dichlorocarbene and Bromine to Olefins

Olefin	Addition of CCl_2^a	Addition of CCl_2^b	Addition of Br_2^c
Cyclohexene	6.29	1.08	1.13
1-Heptene	1.00	1.00	1.00
Vinyltrimethylsilane	0.047 ^{d,5}	0.27 ^e	0.17

^a Dichlorocarbene was generated from chloroform and potassium tert-butyrate, -39°C, n-heptane. ^b Dichlorocarbene was generated by pyrolysis of trichloromethyltrichlorosilane, 235°C, tetrachloromethane. ^c -25°C, n-heptane. ^d -30°C, ^e 200°C.

methylsilylcyclopropane, which decreased the accuracy of chromatographic analysis. In order to exclude the possibility that the results will be affected by different solvation, relative rates of the addition were also measured in *p*-xylene and *n*-heptane; the results presented in Table VII provide evidence that the order of reactivity of the silylolefins is the same in all three types of solvents.

Thermal stability of silyl-substituted dichlorocyclopropanes. With regard to the fact that the addition of the so generated dichlorocarbene is accompanied by some side reactions we have tested thermal stability of silyl-substituted dichlorocyclopropanes in pure state and after the addition of tetrachlorosilane which is always present in reaction mixtures and which, being weak Lewis acid, could catalyze decomposi-

FIG. 1

Dependence of Relative Rate Constant of the Addition of Dichlorocarbene to Vinyltrichlorosilane on Temperature

With respect to 1-heptene; the molar ratio of vinyltrichlorosilane to 1-heptene 15 : 1, tetrachloromethane as solvent, reaction time 20 min.

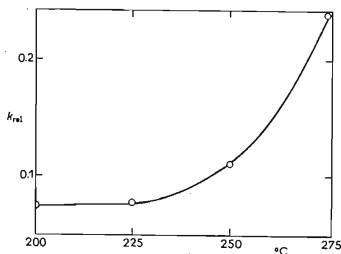


TABLE VII

Relative Rate Constants of the Addition of Dichlorocarbene to Methylchlorosilyl-Substituted Olefins Temperature 200°C, reaction time 20 min.

Olefin	Dibutyl ether		<i>p</i> -Xylene		<i>n</i> -Heptane	
	k_{rel}^a	δ_{max}	k_{rel}^a	δ_{max}	k_{rel}^a	δ_{max}
Vinyltrichlorosilane	0.17	2.4	0.18	2.0	0.21	10.5
Vinylmethylchlorosilane	0.07	7.2	0.15	7.2	0.22	2.7
Vinylmethylchlorosilane	0.34 ^b	1.1	0.36	2.5	0.42	2.5
Vinyltrimethylsilane	0.19 ^b	6.0	0.27	8.9	0.19	3.5
Allylchlorosilane ^c	0.42	13.0	0.74	4.4	0.78	10.2
Allylmethylchlorosilane ^c	2.57	7.0	2.02	7.8	1.49	4.7
Allyldimethylchlorosilane ^c	3.76	0.8	2.36	3.4	2.41	8.3
Allyltrimethylsilane ^c	1.47	10.5	1.32	0	—	—

^a With respect to 1-heptene; the experimental values were not corrected for amounts of thermally decomposed silyldichlorocyclopropanes. ^b Dipropyl ether was used as solvent. ^c Reaction time 60 min.

tion of reaction products. It is known that thermal decomposition of 2-chloroethyl-substituted silanes proceeds at 350–400°C under quantitative elimination of ethylene^{19–21}, 2,2-difluoroethyltrifluorosilane decomposes in a similar way already at 150–200°C²², giving fluoroethylene. By contrast, 3,3,3-trifluoro-substituted propylsilanes undergo decomposition in the region of temperatures 400–500°C^{23,24}. From Table V it is obvious that, in accordance with the expectation, also the dichlorocyclopropanes containing chloro substituents in positions β and γ suffer partial decomposition at 200°C, and that both in pure state and in the presence of silicon tetrachloride. In all the cases the Si—C bond is cleaved under the formation of trimethylchlorosilane (product A, Table IV) in the case of 2,2-dichloro-(1-trimethylsilyl)cyclopropane and dimethyldichlorosilane (product B, Table IV) in the case of the corresponding dimethylchlorosilyl-substituted cyclopropanes. In nearly all cases besides these compounds also an appreciable amount of another compound is formed (product C, Table IV): the determination of the structure of this compound has not been attempted. As estimated from retention time its boiling point is approximately 65°C. As follows from the data given in this table in the presence of silicon tetrachloride dichlorocyclopropane derivatives are cleaved to a greater extent than in the case where the compounds were exposed to high temperature only. Furthermore the dichlorocyclopropanes substituted in position β to silicon by chlorine atoms are more liable to cleavage, compared to those having chlorine atoms in the γ -position. Within each series of the compounds the dependence of relative rate of the addition of dichlorocarbene on the number of chloro substituents cannot be examined in detail due to the cleavage of dichlorocyclopropanes. Notwithstanding, owing to insensitivity of the addition towards solvation effects and the fact that the cleavage of the formed dichlorocyclopropane does not exceed 35 w.%, some general conclusions can however be made.

Allylmethylchlorosilanes, due to the +I effect of the silyl group, are more reactive than 1-heptene, with the exception of allyltrichlorosilane, even though the corresponding dichlorocyclopropane does not decompose on heating or in the presence of tetrachlorosilane. In this case the substitution of the silyl group by three chlorine atoms results in an overall -I effect of trichlorosilyl group, which reflects in a lower reactivity of allyltrichlorosilane, relative to 1-heptane.

In the series of vinylmethylchlorosilanes all the members are markedly less reactive than 1-heptene, which is in harmony with the reactivity of vinylsilanes^{4–6}. The lower reactivity of the vinylmethylchlorosilanes under study is due to a ($p \rightarrow d$) π dative character of the vinyl-silicon bond. Of course, as in the case of the silylmethylchlorosilanes, the effect of substituents attached to silicon on the reactivity of the olefin cannot be quantitatively evaluated because of the above mentioned cleavage of the corresponding dichlorocyclopropane.

With regard to the low stability of silyl-substituted dichlorocyclopropanes towards heat and the chlorosilanes present in the reaction mixture, the addition of the dichloro-

carbene generated by pyrolysis of trichloromethyltrichlorosilane cannot be regarded as a suitable method for quantitative evaluation of the reactivity of olefins towards electrophilic reagents; it is only a semiquantitative method for estimating the reactivity of some silylolefins.

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