VINYL DERIVATIVES OF METALS
XXIV*. CONCERNING THE ADDITION OF DICHLORO- AND DIFLUOROCARBENE VIA THE TRIHALOMETHYL–METAL ROUTE TO VINYL AND ALLYL COMPOUNDS OF CARBON, SILICON AND GERMANIUM

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The relative reactivities of alkyl-substituted olefins toward CCl_2 have been found to decrease with decreasing nucleophilic character of the olefin, *i.e.*, in the order $R_2C=CR_2 > R_2C=CHR > R_2C=CH_2 > RCH=CH_2$. This was the case when dichlorocarbene was generated via the chloroform + base procedure[3], sodium trichloroacetate decarboxylation[4], thermal decomposition of phenyl(bromodichloromethyl)mercury[4] or the $PhHgCCl_3 + NaI$ reagent[5]. These studies suggested that electronic, not steric factors were of prime importance in this obviously electrophilic addition of dichlorocarbene to the C=C bond of olefins. However, in our investigation of the $PhHgCCl_3 + NaI$ system[5], some indication that steric factors do play a role in such reactions was given. Also to be noted in this connection is that Δ^5 double bonds of Δ^5- or $\Delta^{3,5}$-steroids bearing 10 β methyl groups (*e.g.*, Δ^5-androstene-$3\beta,17\beta$-diol diacetate) are completely unreactive toward CCl_2. In contrast, such compounds are reactive to a limited extent toward difluorocarbene and such unsaturated steroids without a 10 β methyl substituent do undergo CCl_2 addition at the Δ^5 double bond[6]. The operation of steric effects clearly is indicated.

With this general background, it is of interest to consider the very low reactivity of vinylsilanes of type $R_3SiCH=CH_2$ toward CCl_2 as generated by the $CHCl_3$ + tert-BuOK procedure at $-30°$[7], and by thermolysis of (trichloromethyl)trichlorosilane[8] and phenyl(bromodichloromethyl)mercury[9]. Table 1 lists results of Cudlín and Chvalovský which illustrate this lack of reactivity. It was the object of the present study to obtain an understanding of the factors (electronic, steric, etc.) which are responsible for this relative inertness of vinylsilanes.

The occurence of π-bonding in vinylsilanes, that is, overlap of the olefinic π electron cloud with vacant d orbitals of silicon in the ground state (Fig. 1), has been invoked in the past by a number of different investigators to explain certain anomalies of vinylsilane reactivity, and spectroscopic investigations (infrared, NMR) have been cited in support of such π-bonding[10–17]. (Note, however, that the vibrational spectra

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TABLE 1

RELATIVE RATES OF CCl_2 (VIA $CHCl_3$ + tert-BuOK AT $-30°$) ADDITION TO SILYL-SUBSTITUTED OLEFINS[7b]

Olefin	k_{rel}
1-Heptene	1.00
$Me_3SiCH=CH_2$	0.047
$Me_3SiOSiMe_2CH=CH_2$	0.033
$(Me_3SiO)_2SiMeCH=CH_2$	0.036
$(Me_3SiO)_3SiCH=CH_2$	0.036
$Me_3SiCH_2CH=CH_2$	5.00

Fig. 1.

of vinyl derivatives of the Group IV elements also have been discussed in terms of the absence of important π-bonding effects[18]). Thus a decrease in the nucleophilicity of the C=C bond in the $R_3SiCH=CH_2$ compounds due to such π-overlap could serve to explain their observed poor reactivity toward dichlorocarbene, and such an explanation was favored by the Czechoslovak workers[7]. However, the possibility that steric effects were in large part responsible for this inertness must also be considered, since in each case studied the silicon atom to which the vinyl group was attached had three other, relatively bulky substituents (cf. Table 1). The absence of suitable control experiments left open the question as to which factor, C$\rightarrow$Si π-bonding or a steric effect, bore major responsibility for the inertness of vinylic silanes toward CCl_2. An attempt has been made in the present study to answer this question by means of an approach involving the comparative organic chemistry of carbon and silicon[19].

We have compared relative rates of addition of dichlorocarbene as generated by thermolysis of phenyl(bromodichloromethyl)mercury* to vinyl derivatives of carbon, silicon and germanium with k_{rel} for CCl_2 addition to allyl derivatives of these elements. The results are given in Table 2. The general procedure of our previous study of olefin reactivities toward dichlorocarbene[4] was used. Each olefin in Table 2 was allowed to compete with an equimolar amount of a reference olefin for a deficiency of phenyl(bromodichloromethyl)mercury. Upon completion of the reaction, the amounts of gem-dichlorocyclopropane produced from the olefin under investigation and the reference olefin were determined by gas-liquid partition chromatography (GLPC), and the relative rate for each olefin was calculated by the method of Doering

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* The $PhHgCCl_2Br$ + olefin reaction involves the following mechanism[20]:

$$PhHgCCl_2Br \underset{k_{-1} (fast)}{\overset{k_1 (slow)}{\rightleftharpoons}} PhHgBr + CCl_2$$
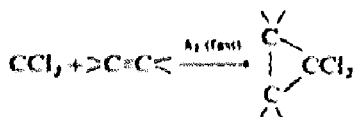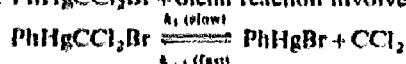
TABLE 2

RELATIVE REACTIVITIES OF GROUP IV-SUBSTITUTED OLEFINS TOWARD PHENYL-(BROMODICHLOROMETHYL)-MERCURY-DERIVED DICHLOROCARBENE

Olefin	k_{rel}	Temp. (°C)
1-Heptene	1.00	80
CCl_2=CHCl	0.14	80
$C_2H_5(CH_3)_2CCH$=CH_2	0.043	80
$C_2H_5(CH_3)_2SiCH$=CH_2	0.069	80
$(C_2H_5)_3SiCH$=CH_2	0.048	80
$(C_2H_5)_3GeCH$=CH_2	0.064	80
$(CH_3)_3CCH_2CH$=CH_2	0.78	71
$(CH_3)_3SiCH_2CH$=CH_2	4.2	71
$(CH_3)_3GeCH_2CH$=CH_2	5.7	71

and Henderson[3]. Separate experiments established the reliability of this procedure. The *gem*-dichlorocyclopropanes produced by CCl_2 addition to the olefins listed in Table 2 were fully characterized in separate experiments and have been the subject of a previous paper from these Laboratories[21]. The competition reactions which provided these data were carried out at 80° with the vinyl derivatives, at 71° with the allyl derivatives. In the case of the vinyl compounds the reference olefin used was trichloroethylene; for the allyl compounds cyclohexene was used, but for convenience, all k_{rel} values were calculated with respect to k_{rel} (1-heptene) = 1. A separate competition experiment with 1-heptene and trichloroethylene was required for this purpose, and the results of a competition of $Me_2EtSiCH$=CH_2 and 1-heptene for mercurial-derived CCl_2 [$k(Me_2EtSiCH$=$CH_2)/k(1$-heptene$)$=0.07] demonstrated the validity of these calculations. To obtain k_{rel} of the olefins in Table 2 vs. cyclohexene, the reference olefin of our previous study[4], the k_{rel} values of Table 2 should be multiplied by 0.236. Thus we find, for instance, that $Me_2EtSiCH$=CH_2 is only 0.016 times as reactive as cyclohexene.

The relative reactivities listed in Table 2 now make possible an assessment of the factors which affect the reactivity of vinylsilanes toward dichlorocarbene. In the case of the allyl compounds, where the quaternary center is separated from the C=C bond undergoing attack by CCl_2 by a methylene group, it is apparent that steric factors are not very important. This is shown by the fact that Me_3CCH_2CH=CH_2 is only slightly less reactive toward CCl_2 than is 1-heptene (cf. Table 2). Thus, as a first approximation, we can ascribe the consequences of replacing the tert-butyl group by a trimethylsilyl group and then by a trimethylgermyl group in the allyl derivatives to the operation of electronic factors. It has been shown that the order of increasing $(+I)$ inductive effect for Me_3M^{IV} groups is $Me_3C < Me_3Si < Me_3$-Ge^{22-24} and our observed k_{rel} values for the Group IV allyltrimethyl compounds provide further confirmation for this.

We now consider the vinyl derivatives of carbon and silicon listed in Table 2. Me_2EtCCH=CH_2 is only 0.04 times as reactive toward electrophilic attack by dichlorocarbene as 1-heptene, and this must be ascribed to very severe steric hindrance by the three alkyl substituents on the carbon atom attached to the C=C bond. Molecular models confirm this; the C–H bonds of the Me_2EtC group drastically reduce the accessibility of the C=C bond system to attacking CCl_2. Electronic effects

clearly are not important. If only inductive effects were operative in determining the difference in k_{rel} between $Me_2EtCCH=CH_2$ and $Me_2EtSiCH=CH_2$, to the exclusion of π-bonding and steric effects, then we should expect the latter to be ca. five times more reactive toward CCl_2 than the former. However, the covalent radius of silicon is 1.17 Å, while that of carbon is 0.77 Å. The consequence of this increase in size should be that the three alkyl substituents on the silicon atom should provide *less* hindrance to CCl_2 approach to the C=C bond. This is shown by inspection of molecular models: due to the longer Si–C bond (compared to the C–C bond), the ethyl and methyl hydrogens of the Me_2EtSi group do not shield the C=C bond as effectively as do those of the Me_2EtC group. It is not possible to assess this steric factor quantitatively, and we can only say that on the basis of steric factors alone, $Me_2EtSiCH=CH_2$ should be more reactive than $Me_2EtCCH=CH_2$. Considering both the $+I$ and steric effects in these olefins, we estimate that $k_{rel}(Me_2EtSiCH=CH_2)/k_{rel}(Me_2EtCCH=CH_2) \geqslant 10$. In our competition study we found this ratio to be 1.6, a fact which suggests that still another factor must be considered, one that serves to decrease the reactivity of the vinylsilicon compound. We suggest, in agreement with Cudlin and Chvalovský[7], that C$\rightarrow$Si π-bonding provides a reasonable and adequate explanation for this observation. However, even in the absence of such a π-bonding effect we would expect $Me_2EtSiCH=CH_2$ to be less reactive than 1-heptene, due to the operation of steric factors. We thus suggest that the very low reactivity of $R_3SiCH=CH_2$ compounds *relative to 1-heptene* is a result of both the steric factor associated with the three R groups on silicon and a very significant decrease in the nucleophilicity of the C=C bond due to C$\rightarrow$Si π overlap as shown in Fig. 1. The relative importance of these effects cannot be assessed. The steric effect would be eliminated in $H_3SiCH=CH_2$, but since CCl_2 readily undergoes insertion into Si–H bonds (at a rate comparable to its addition to the C=C bond of cyclohexene)[25], experiments with this olefin are not feasible.

Little change in reactivity toward dichlorocarbene was observed on going from $Me_2EtSiCH=CH_2$ to $Et_3SiCH=CH_2$ to $Et_3GeCH=CH_2$. It is perhaps noteworthy that $k_{rel}(Ge)/k_{rel}(Si)$ for the respective vinyl and allyl derivatives are virtually identical. This could be taken as an indication that the changes in the steric factors and the π-bonding effects on going from vinylsilicon to vinylgermanium compounds are not of great importance and that the inductive effect plays the major role. However, the interplay of these three factors need not be as simple as that. It may, however, be noted that the increase in covalent radius on going from silicon (1.17 Å) to germanium (1.22 Å) is not large, and that C$\rightarrow$M^{IV} π-bonding apparently is less important in the case of organogermanium compounds than it is in organosilicon compounds[26].

Attempts to include allyl- and vinyltin compounds in this study were not successful, since the $PhHgCCl_2Br$ + allyl- or vinyltin reaction is complicated by cleavage of allyl and vinyl groups from tin by the PhHgBr formed in the CCl_2 extrusion step[21].

This investigation also included a study of relative reactivities of vinyl derivatives of carbon, silicon and germanium toward difluorocarbene as generated by the Me_3SnCF_3 + NaI reagent in 1,2-dimethoxyethane at 80°[27], since it was of interest to examine the effect of a decrease in the steric requirements of the attacking carbene. Table 3 shows the k_{rel} values obtained. The fact that, with respect to the reference olefin, $Me_2EtCCH=CH_2$ is three times more reactive toward CF_2 than toward CCl_2

TABLE 3

RELATIVE REACTIVITIES OF VINYLSILICON AND -CARBON COMPOUNDS TOWARD DIFLUOROCARBENE, IN DME
AT 80°

Olefin	k_{rel}
1-Heptene	1.0
$Me_2EtCCH=CH_2$	0.12
$Me_2EtSiCH=CH_2$	0.26
$Et_3SiCH=CH_2$	0.15

can be ascribed to the smaller size of the former. Note, however, that for the Me_2Et-$MCH=CH_2$ compounds the $k_{rel}(Si)/k_{rel}(C)$ ratios for CF_2 (2.2) and CCl_2 (1.6) differ much less; this again can be rationalized in terms of the operation of π-bonding effects in the vinylsilane.

An attempt was made to measure the relative reactivities of $Me_2EtCCH=CH_2$ and $Me_2EtSiCH=CH_2$ toward the much larger dibromocarbene as generated from phenyl(tribromomethyl)mercury. However, control experiments showed that the resulting gem-dibromocyclopropanes appeared to undergo partial decomposition under the conditions of reaction and/or analysis, and for this reason no meaningful data could be obtained.

In summary, the results of this assessment of the relative reactivities of analogous vinyl derivatives of carbon, silicon, and germanium appear to provide further chemical evidence in support of that derived largely from spectroscopic studies that $C \rightarrow M^{IV}$ π-bonding contributes to the ground state description of vinylsilanes and (less clearly) vinylgermanes. It should be noted, however, that such a conclusion was only justified when the appropriate control experiments involving analogous compounds of carbon had been made.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen. Benzene was distilled from calcium hydride, DME from potassium immediately before use.

For the quantitative GLPC analyses in this study an F&M Model 700 gas chromatograph was used; the column packing was either 15% General Electric Co. XE-60 on Chromosorb P or 20% General Electric Co. SE-30 on Chromosorb W, with a 60–250° temperature program, generally 10°/min.

All the gem-dichlorocyclopropanes[21] and gem-difluorocyclopropanes[27] were fully characterized and have been reported by us previously.

Competition reactions using phenyl(bromodichloromethyl)mercury

The general procedure was as follows. Phenyl(bromodichloromethyl)-mercury[28] (5 mmoles), the olefin under investigation and the reference olefin (25 mmoles each) and 10 ml of benzene were charged into a 50 ml, three-necked flask equipped with a reflux condenser topped with a nitrogen inlet tube, a thermometer and a magnetic stirring assembly. The flask was immersed in an oil bath maintained at 80° ±0.5° and stirred for 4 h. The reaction mixture then was allowed to cool to

TABLE 4

COMPETITION REACTIONS WITH PHENYL(BROMODICHLOROMETHYL)MERCURY

Olefin "a"	CCl_2 adduct with olefin "a" (%)	Yield of CCl_2 adduct with reference olefin (%)	Total yield (%)	k_a/k_{ref}	k_a/k_{ref} (average)
Vinyl derivatives; reference olefin is trichloroethylene					
$Me_2EtCCH=CH_2$	21.0 (22.2)[a]	72.4 (72.0)	93.4 (94.2)	0.29 (0.31)	0.30
$Me_2EtSiCH=CH_2$	26.9 (26.4)	54.9 (55.1)	81.8 (81.5)	0.47 (0.48)	0.475
$Et_3SiCH=CH_2$	18.2 (18.1; 20.8)	56.4 (63.3; 55.0)	74.6 (81.4; 75.8)	0.32 (0.29; 0.38)	0.33
$Et_3GeCH=CH_2$	25.1 (22.2; 21.3)	53.6 (56.0; 69.5)	78.7 (78.2; 90.8)	0.47 (0.40; 0.44)	0.44
$n\text{-}C_5H_{11}CH=CH_2$	76.6 (77.2)	11.2 (11.1)	87.8 (88.3)	6.84 (6.95)	6.90
Allyl derivatives; reference olefin is cyclohexene					
$Me_3CCH_2CH=CH_2$	10.5 (13.2; 13.6)	68.0 (67.2; 64.0)	78.5 (80.4; 77.6)	0.15 (0.19; 0.21)	0.18
$Me_3SiCH_2CH=CH_2$	39.8 (42.2; 41.4)	39.3 (42.7; 42.4)	79.1 (84.9; 83.8)	1.04 (0.98; 0.97)	1.0
$Me_3GeCH_2CH=CH_2$	50.6 (50.0)	38.4 (36.3)	89.0 (86.3)	1.32 (1.37)	1.35

[a] Results of duplicate and triplicate runs are given in parentheses.

room temperature, an accurately weighed quantity of an internal standard (usually ethylbenzene) was added, and all volatiles were trap-to-trap distilled (0.03 mm, bath at 100°) into a receiver at −78°. Response factors of the reaction products relative to the internal standard had been determined in separate experiments GLPC analysis of the distillate followed. All reactions were carried out in duplicate, some in triplicate. The relative rates were calculated using the equation[3]

$$k_{rel} = k_a/k_{ref} = P_a/P_{ref} \times O_{ref}/O_a$$

where k_a = rate constant of the olefin under investigation, k_{ref} = rate constant of the reference olefin, P_a and P_{ref} = mmoles of products derived from the olefin under investigation and the reference olefin, respectively, and O_a and O_{ref} = initial mmoles of the olefin under investigation and the reference olefin, respectively. The results of these experiments are given in Table 4.

Competition experiments using the Me_3SnCF_3 + NaI reagent

Five mmoles each of trimethyl(trifluoromethyl)tin[29] and sodium iodidide

TABLE 5

COMPETITION REACTIONS WITH THE Me_3SnCF_3 + NaI REAGENT[a]

Olefin "a"	Olefin "a"-derived difluorocyclopropane, yield (%)	1,1-Difluoro-2-n-amylcyclopropane, yield (%)	Total yield (%)	k_a/k_{ref}	k_a/k_{ref} (average)
$Me_2EtCCH=CH_2$	6.0 (6.6)[b]	51.4 (55.0)	57.4 (61.0)	0.117 (0.121)	0.12
$Me_2EtSiCH=CH_2$	12.6 (12.8)	53.0 (51.0)	65.6 (63.8)	0.248 (0.263)	0.26
$Et_3SiCH=CH_2$	6.9 (6.7)	47.4 (46.9)	54.3 (53.6)	0.146 (0.144)	0.15

[a] Reference olefin was 1-heptene. [b] Results of duplicate runs are given in parentheses.

[powdered and dried at 110° (0.01 mm) for 24 h], 25 mmoles each of the olefin under investigation and the reference olefin and 10 ml of DME (distilled from potassium directly into the reaction flask) were used. The reaction mixture was heated with stirring under nitrogen for 20 h at 80° ±0.5°. The further operations were as described in the experiment above. The results are given in Table 5.

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SUMMARY

Vinyl derivatives of silicon are known to be very unreactive toward dichlorocarbene. A study of the relative reactivities of selected vinyl and allyl derivatives of carbon, silicon and germanium toward PhHgCCl$_2$Br-derived dichlorocarbene gave results which are rationalized in terms of a decrease in the nucleophilicity of the C=C bond of vinylsilanes, caused by π-overlap between the filled olefinic π orbital and vacant silicon d orbitals, contributing significantly to this lack of reactivity. However, it is suggested that steric hindrance to CCl$_2$ attack at the C=C bond in vinylsilanes by the three other substituents on silicon also is of importance.

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