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EFFECT OF THE CATION IN THE REGIOSELECTIVITY CONTROL IN REACTIONS OF 3,3-DICHLOROALLYL METALS WITH SUBSTITUTED BENZALDEHYDES

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Abstract

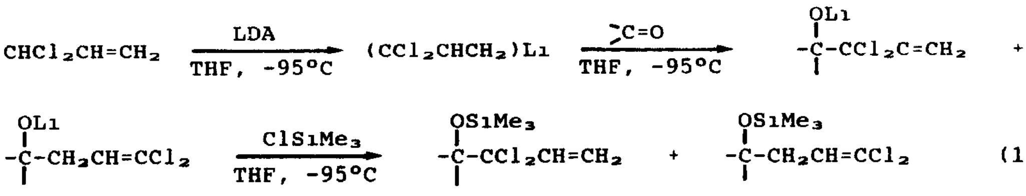
gem-Dichloroallyl-lithium and *gem*-dichloroallyl-potassium, produced respectively upon treatment of 3,3-dichloropropene with lithium diisopropylamide alone or in the presence of potassium *tert*-butoxide, show opposite regioselectivity in the reactions with substituted benzaldehydes.

Introduction

The regiochemical result of reactions of unsymmetrically substituted allylic carbanions comes from many factors[1] and new methods to control the regioselectivity are useful both from the synthetical and theoretical point of view. These anionic species react with electrophiles to give products that are characteristic of the reaction at either or both termini of the propenylic system. Seyferth and coworkers have investigated the reaction of *gem*-dichloroallyl-lithium, obtained by the action of *n*-butyllithium on 3,3-dichloroallyltriphenyl-lead in THF at -95 °C, with several organic substrates.[2] The reactions of chloroallyl-lithium and *gem*-chloro(methyl)allyl-lithium with different electrophiles, and their synthetic utility have been diffusely studied by Mauze' and coworkers.[3] A convenient procedure for controlling the regioselectivity of the alkoxy and alkylthio substituted allylic carbanions *via* aluminum "ate" complexes has been reported by Yamamoto and coworkers.[4] Schlosser and coworkers have extensively studied organo-metallic compounds generated through metallation with *n*-butyllithium in the presence of potassium *tert*-butoxide, focusing their attention on the stereoselective and regioselective behaviour.[5]

Here we report a procedure for controlling the regiochemistry of the reaction of *gem*-dichloroallyl anion with some carbonyl compounds, that is realized by producing the 3,3-dichloropropenide with lithium diisopropylamide (LDA) in the presence of potassium *tert*-butoxide.

Results and Discussion



$$\mathrm{CHCl_2CH{=}CH_2} \xrightarrow[\mathrm{THF,\ -95^{\circ}C}]{\mathrm{LDA}} \mathrm{(CCl_2CHCH_2)Li} \xrightarrow[\mathrm{THF,\ -95^{\circ}C}]{\mathrm{>C{=}O}} -\overset{\mathrm{OLi}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\mathrm{CCl_2C{=}CH_2} \; + \; -\overset{\mathrm{OLi}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\mathrm{CH_2CH{=}CCl_2} \xrightarrow[\mathrm{THF,\ -95^{\circ}C}]{\mathrm{ClSiMe_3}} -\overset{\mathrm{OSiMe_3}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\mathrm{CCl_2CH{=}CH_2} \; + \; -\overset{\mathrm{OSiMe_3}}{\overset{|}{\underset{|}{\mathrm{C}}}}-\mathrm{CH_2CH{=}CCl_2} \qquad (1)$$

In Table 1 are reported the results obtained according to equation 1 with different aromatic aldehydes when the addition to the C=O group is carried out in the absence of potassium *tert*-butoxide.

Table 1. Reactions of 3,3-dichloropropene with some carbonyl compound in the presence of LDA[a]

Carbonyl compd.	Yield[b] (%)	$CCl_2:CH_2$[c] Ratio
PhCHO	80[d]	15:85
p-$CF_3C_6H_4CHO$	75	<1:100
o-ClC_6H_4CHO	65	<1:100
p-ClC_6H_4CHO	73	<1:100
o-$MeOC_6H_4CHO$	68	<1:100
p-$MeOC_6H_4CHO$	75[d]	23:77
o-MeC_6H_4CHO	63	<1:100
p-MeC_6H_4CHO	68	<1:100

a: 3,3-dichloropropene, 2.5 mmol; carbonyl compound, 2.5 mmol; LDA, 2.5 mmol; THF, 20 ml; T= -95 °C. *b*: isolated product, the missing material consists of unreacted aldehyde. *c*: by ^1H *n.m.r.* on the crude reaction product (±5%). *d*: total yield.

The data indicate that the tested carbonyl compounds preferentially react at the CH_2 terminus of the *gem*-dichloroallyl-lithium: in fact only benzaldehyde and 4-methoxybenzaldehyde afford a reaction mixture corresponding to the attack at both termini of the propenylic system ($CCl_2:CH_2$ ratio = 15:85, 23:77 respectively). All the other substituted benzaldehydes react at the CH_2 terminus of the *gem*-dichloroallyl-lithium.

Similar results for *para* and *meta* substituted acetophenones have been rationalized by Seyferth[2b] in terms of Pearson's hard-soft acid-base (HSAB)[6] theory. According to this approach the CH_2 terminus of *gem*-dichloroallyl anion is the hard nucleophilic site and as such preferentially reacts with hard electrophiles. Hard electrophiles should be considered carbonyl compounds with electron-withdrawing substituents which contribute to harden the C=O function.

The regiochemical behaviour of benzaldehydes substituted with electron-withdrawing groups that form the new C-C bond at the CH_2 terminus of the 3,3-dichloropropenide could be appropriately set in this frame. In accordance with these considerations might also appear the reactions of benzaldehyde and 4-methoxy-benzaldehyde that afford a higher percentage of attack at the CCl_2 site. More contradictory with the HSAB theory are the other results in Table 1 obtained for benzaldehydes substituted with electron-releasing groups.

Table 2. Reactions 3,3-dichloropropene with benzaldehyde in the presence of LDA as a function of the equivalents of potassium tert-butoxide[a]

Yield[b] (%)	CCl_2:CH_2[c] Ratio	*t*-BuOK Equiv.
80[d]	15:85	0
78[d]	30:70	0.50
78[d]	74:26	0.75
70[d]	90:10	1.00
70	100:<1	1.25

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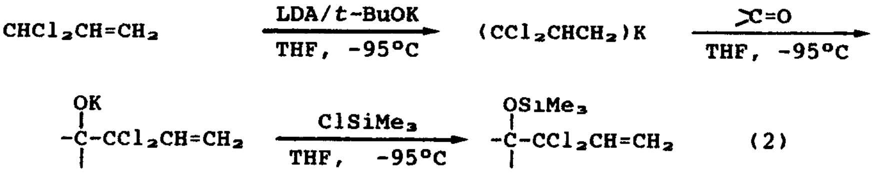
a: 3,3-dichloropropene, 2.5 mmol; carbonyl compound, 2.5 mmol; LDA, 2.5 mmol;THF, 20 ml; T= -95 °C. *b*: isolated product, the missing material consists of unreacted aldehyde. *c*: by ^1H *n.m.r.* on the crude reaction product (±5%). *d*: total yield.

We think that it would be inadequate to explain the preferential reaction at the CH_2 terminus as a simple consequence of the steric repulsion between the two chlorine atoms at the CCl_2 site and the carbonyl compound. In such a case steric requirement should as well control the reaction regiochemistry in the presence of potassium *tert*-butoxide: in fact the steric hindrance of the CCl_2 group has not to be different in the metallated species $(CCl_2CHCH_2)Li$ and $(CCl_2CHCH_2)K$. Moreover the anion approaches the electrophil centre orthogonal to the plane containing substituents.

The results reported in Table 2 indicate that the CCl_2 terminus becomes progressively the preferential reaction site with benzaldehyde, if the metallation reaction is carried out with LDA in the presence of increasing amounts of potassium *tert*-butoxide.

According to these results, the data in Table 3 indicate that all the tested carbonyl compounds react with the CCl_2 site in the presence of potassium *tert*-butoxide according to equation 2, independently of the electron releasing or withdrawing properties of the substituents in the *ortho* or *para* positions.



$$\mathrm{CHCl_2CH{=}CH_2} \xrightarrow[\mathrm{THF,\ -95^{\circ}C}]{\mathrm{LDA}/t\text{-}\mathrm{BuOK}} \mathrm{(CCl_2CHCH_2)K} \xrightarrow[\mathrm{THF,\ -95^{\circ}C}]{\mathrm{{>}C{=}O}}$$

$$-\overset{\mathrm{OK}}{\underset{|}{\overset{|}{\mathrm{C}}}}-\mathrm{CCl_2CH{=}CH_2} \xrightarrow[\mathrm{THF,\ \ -95^{\circ}C}]{\mathrm{ClSiMe_3}} -\overset{\mathrm{OSiMe_3}}{\underset{|}{\overset{|}{\mathrm{C}}}}-\mathrm{CCl_2CH{=}CH_2} \qquad (2)$$

Table 3. Reactions 3,3-dichloropropene with some carbonyl compounds in the presence of LDA and of potassium tert-butoxide[a]

Carbonyl compd.	Yield[b] (%)	$CCl_2:CH_2$[c] Ratio
PhCHO	70	100:<1
p-$CF_3C_6H_4CHO$	65	100:<1
o-ClC_6H_4CHO	60	100:<1
p-ClC_6H_4CHO	67	100:<1
o-$MeOC_6H_4CHO$	63	100:<1
p-$MeOC_6H_4CHO$	65	100:<1
o-MeC_6H_4CHO	60	100:<1
p-MeC_6H_4CHO	68	100:<1

a: 3,3-dichloropropene, 2.5 mmol; carbonyl compound, 2.5 mmol; LDA, 2.5 mmol; *t*-BuOK, 3.12 mmol; THF, 20 ml; T = -95 °C. *b*: isolated product, the missing material consists of unreacted aldehyde. *c*: by ^1H *n.m.r.* on the crude reaction product (±5%).

Schlosser[7] and Lochmann[8] have reported that organopotassium compounds can be prepared by treatment of organolithium derivatives with potassium alkoxides. According to these results the metallation of 3,3-dichloropropene with LDA in the presence of potassium *tert*-butoxide should lead to the formation of *gem*-dichloroallyl-potassium instead of the the *gem*-dichloroallyl-lithium obtained by lithium-hydrogen exchange with LDA alone. Since the carbonyl compounds react in the two cases with two different allylmetal species it is important to consider the variety of forms in which these reacting ionic species can exist in solution:[9] *e.g.* tight or loose ion pairs, solvent separated ion pairs, monomers and dimers.

In this respect, Schleyer[10] has carried out cryoscopic measurements and ^{13}C n.m.r. studies that show that allyllithium is a unsymmetrical dimer in THF at -108 °C at a concentration of 0.097 mol/l; MNDO calculation of the geometries for allyl-lithium dimers show the bridging lithium closer to one of the two CH_2 termini. These experimental conditions are very close to those of our reactions: -95 °C, 0.1 mol/l. On the contrary allyl-sodium and allyl-potassium derivatives can be presumably expected to be monomeric in THF.[11]

The equilibrium between tight ion pairs and loose ion pairs (solvent-separated ion pairs) is known to be strongly affected by the nature of the cation. Solvation of larger cations is weak, and the fraction of solvent-separated ion pairs decreases, while with smaller cations strong solvation shells lead to solvent-separated ion pairs. Usually, the proportion of separated ion pairs decreases along the series Li, Na, K, Cs.[12]

According to these reports we may suppose that in the case in which the reaction conditions lead to $(CCl_2CHCH_2)Li$ (metallation carried out with LDA alone - Equation 1) the electrophile might react with a monomer in which the lithium counterion interacts with both termini of the propenylic system[13] or, consistently with the data reported by Schleyer for unsubstituted allyl anion, with a dimer where the two lithium cations unsymmetrically engages both termini of two 3,3-dichloropropenide moieties.

This hypothesis is consistent with the regiochemical results obtained with $(CCl_2CHCH_2)Li$, that show the products corresponding to the addition to either termini of the allylic system or exclusively to the CH_2 site.

In the case in which the reaction conditions lead to $(CCl_2CHCH_2)K$ (metallation carried out with LDA in the presence of potassium *tert*-butoxide - Equation 2) carbonyl compounds should react with a monomer in which the potassium counterion is less solvated by THF and more tightly bonded to the CCl_2 terminus of 3,3-dichloropropenide (with respect to lithium in the corresponding system). Such a situation should entail that *gem*-dichloroallyl-potassium offers the CCl_2 site with a more localized charge as a consequence of the more tight ion pair. According to this hypothesis $(CCl_2CHCH_2)K$ should add to the carbonyl group with a marked preference for the CCl_2 terminus, as experimentally found in our regiochemical results.

The counterion could even play a more important role in the regiochemical control in connection with its participation to the transition structure which has been examined from a computational point of view by Schleyer for a model reaction of formaldehyde with the monomer of methyl-lithium, as well with its dimer.[15] In the proposed reaction pathway the carbonyl oxygen strongly interacts with lithium before the formation of the new C-C bond, providing a four-center transition structure.

In the present case the lithiated species, both monomer and dimer, that show the cation interacting with both termini of 3,3-dichloropropenide, can participate to similar transition structure whether the reaction occurs to the CCl_2 site or to the CH_2 one. On the contrary, if *gem*-dichloroallyl-potassium is really present as a monomer with the potassium strongly engaged with the CCl_2 terminus, carbonyl group will be forced to react with such site by the C=O··K interaction that precedes the formation of the new C-C bond.

Experimental

All the reactions of gem-dichloroallyl-lithium were carried out under argon atmosphere in flame dried glassware. THF was dried by distillation from sodium benzophenone ketyl directly into the reaction vessel under inert atmosphere. The reaction temperature is uncorrected: it was measured using a pentane (total immersion) thermometer immersed to a depth of about 15 cm in the refrigerating bath. *n*-Butyllithium (1.6 M solution in hexanes) and diisopropylamine were purchased from Aldrich, potassium *tert*-butoxide from Merck, and was sublimated under vacuum (0.1 Torr) prior to the reaction. The carbonyl compounds were commercial and were used without further purification. 3,3-Dichloropropene was synthetized according to the literature.[16] ^1H N.m.r spectra were recorded on a Hitachi Perkin-Elmer R-24B 60 MHz high resolution spectrometer using TMS as internal standard. MS spectra were recorded at 70 eV with a HP 5970 B mass selective detector connected to a HP 5890 GC; cross-linked methyl silicone capillary column. Preparative column chromatography were carried out on silica gel Merck Kieselgel 60 with diethyl ether-petroleum ether (40-70) as an eluant (3:97).

In Situ Reaction Procedure. The standard apparatus for the reactions of gem-dichloroallyl-lithium generated *in situ* by lithium-hydrogen exchange consisted of a 200 ml Schlenk bottle capped with a rubber septum, equipped with a teflon covered stirring bar and connected to an argon line. The apparatus was maintained at low temperatures by placing it in a Dewar flask filled with acetone cooled to its freezing point (-95 °C) with liquid nitrogen.

Method A - Reaction Carried out with LDA. 1.6 ml (2.5 mmol) of *n*-butyllithium (1.6 M solution in hexanes) were added dropwise with a syringe to 20 ml of dry THF, previously cooled at -20 °C. Subsequentely a mixture of diisopropylamine (0.25 g ,2.5 mmol) and of anhydrous THF (1 ml) is added dropwise;[17] after a few minutes the flask was cooled at -95 °C and allowed to stand for 15 min for equilibrating the temperature. 3,3-Dichloropropene (0.27 g, 2.5 mmol) mixed with the desired carbonyl compound (2.5 mmol) (dissolved in 1.0 ml of anhydrous THF) were added dropwise under stirring within 5 min with a syringe to this solution. The reaction mixture was then stirred for 2 h under argon at -95 °C. After the addition of $ClSi(CH_3)_3$ (0.5 ml, 3.9 mmol) at that temperature, the reaction mixture was allowed to reach room temperature, then was poured in water. The organic layer was separated and the aqueous one extracted twice with diethyl ether (15 ml). The combined organic phases were washed with water (10 ml) and dried with anhydrous Na_2SO_4. The solution was condensed under reduced pressure and the residue was analysed by ^{1}H *n.m.r.* spectroscopy, in order to establish the CCl_2:CH_2 ratio. The obtained products have been purified by column chromatography and successively distilled with a Kugelrohr apparatus. All the products distilled between 80-90 °C (dial type thermometer) at 0.1 Torr.

Method B - Reaction Carried out with LDA in the Presence of Potassium tert-Butoxide. LDA (2.5 mmol) was prepared according to *Method A* and then potassium *tert*-butoxide (0.35 g, 3.12 mmol) was added to the flask cooled at -95 °C. The reaction afterwards proceeds according to the procedure reported in *Method A*.

Table 4. Products characterization.

Compound (n_D^{20})

PhCH(OSiMe$_3$)CH$_2$CH=CCl$_2$ (1.5053) MS, *m/e* (relative intensity) 179 (75), 128 (10), 75 (24),73(100); ^{1}H *n.m.r.* δ (CCl_4) 0.02 (s, 9H, -Si(C*H*$_3$)$_3$); 2.47 (dd, 2H, -C*H*$_2$CH=CCl$_2$); 4.63 (t, J= 6Hz, 1H, C$_6$H$_5$-C*H*); 5.77 (t, J= 7Hz, 1H, -C*H*=CCl$_2$); 7.20 (m, 5H, C$_6$*H*$_5$). Calcd for $C_{13}H_{18}Cl_2OSi$: C, 53.97; H, 6.27. Found: C, 53.87; H, 6.50.

PhCH(OSiMe$_3$)CCl$_2$CH=CH$_2$ (1.5089) MS, *m/e* (relative intensity) 237 (1), 201 (5), 179 (75), 128 (12), 93 (12), 75 (11), 73 (100); ^{1}H *n.m.r.* δ (CCl_4) 0.05 (s, 9H, -Si(C*H*$_3$)$_3$); 4.95 (s, 1H, C*H*CCl$_2$); 5.30 (dd, J= 10 Hz, 1Hz, 1H, HC=CH*H* *cis*); 5.60 (dd, J= 16 Hz, 1Hz, 1H, HC=CH*H* *trans*); 6.25 (dd, J= 10 Hz, 16 Hz, 1H, *H*C=CH$_2$); 7.40 (m, 5H, C$_6$*H*$_5$).Calcd for $C_{13}H_{18}Cl_2OSi$: C, 53.97; H, 6.27. Found: C, 53.80; H, 6.44.

***p*-CF$_3$C$_6$H$_4$CH(OSiMe$_3$)CH$_2$CH=CCl$_2$** (1.4719) MS, *m/e* (relative intensity) 247 (25), 155 (15), 75 (13), 73 (100); ^{1}H *n.m.r.* δ (CCl_4) 0.05 (s, 9H, -Si(C*H*$_3$)$_3$); 2.45 (dd, 2H, -C*H*$_2$CH=CCl$_2$); 4.77 (t, J= 6Hz, 1H, -C$_6$H$_4$C*H*); 5.80 (t, J= 7Hz, 1H, -C*H*=CCl$_2$);7.25-7.60 (m, 4H, C$_6$*H*$_4$). Calcd for $C_{14}H_{17}Cl_2F_3OSi$: C, 47.06; H, 4.80. Found: C, 47.51; H, 4.90.

***p*-CF$_3$C$_6$H$_4$CH(OSiMe$_3$)CCl$_2$CH=CH$_2$** (1.4766) MS, *m/e* (relative intensity) 305 (2), 269 (2), 247 (49), 155 (22), 93 (19), 75 (12), 73 (100); ^{1}H *n.m.r.* δ (CCl_4) 0.08 (s, 9H, -Si(C*H*$_3$)$_3$); 4.93 (s, 1H, C*H*CCl$_2$); 5.25 (dd, J= 10 Hz, 1Hz, 1H, HC=CH*H* *cis*); 5.47 (dd, J= 16 Hz, 1Hz, 1H, HC=CH*H* *trans*); 6.15 (dd, J= 10 Hz, 16 Hz, 1H, *H*C=CH$_2$); 7.47 (s, 4H, C$_6$*H*$_4$). Calcd for $C_{14}H_{17}Cl_2F_3OSi$: C, 47.06; H, 4.80. Found: C, 46.90; H, 4.94.

_o_-ClC$_6$H$_4$CH(OSiMe$_3$)CH$_2$CH=CCl$_2$ (1.5128) MS, *m/e* (relative intensity) 213 (48), 93 (10), 75 (37), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.04 (s, 9H, -Si(CH_3)$_3$); 2.43 (dd, 2H, -CH_2CH=CCl$_2$); 5.07 (t, J= 6Hz, 1H, -C$_6$H$_4$-CHCH$_2$); 5.83 (t, J= 7Hz, 1H,-CH=CCl$_2$); 7.03-7.30 (m, 4H, C$_6\mathit{H}_4$). Calcd for C$_{13}$H$_{17}$Cl$_3$OSi: C, 48.23; H, 5.29. Found: C, 48.61; H, 5.38.

_o_-ClC$_6$H$_4$CH(OSiMe$_3$)CCl$_2$CH=CH$_2$ (1.5043) MS, *m/e* (relative intensity) 213 (63), 75 (11), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.09 (s, 9H, -Si(CH_3)$_3$); 5.15 (dd, J= 10 Hz, 1Hz, 1H, HC=CHH *cis*); 5.40 (dd, J= 16 Hz, 1Hz, 1H, HC=CHH *trans*); 5.40 (s, 1H, CHCCl$_2$); 6.10 (dd, J= 10 Hz, 16 Hz, 1H, HC=CH$_2$); 7.05 (m, 4H, C$_6\mathit{H}_4$). Calcd for C$_{13}$H$_{17}$Cl$_3$OSi: C, 48.23; H, 5.29. Found: C, 48.70; H, 5.10.

_p_-ClC$_6$H$_4$CH(OSiMe$_3$)CH$_2$CH=CCl$_2$ (1.5159) MS, *m/e* (relative intensity) 213 (49), 75 (39), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.05 (s, 9H, -Si(CH_3)$_3$); 2.40 (dd, 2H, -CH_2CH=CCl$_2$); 4.60 (t, J= 6Hz, 1H, -C$_6$H$_4$-CH); 5.70 (t, J= 7Hz, 1H, -CH=CCl$_2$); 7.13 (s, 4H, C$_6\mathit{H}_4$). Calcd for C$_{13}$H$_{17}$Cl$_3$OSi: C, 48.23; H, 5.29. Found: C, 48.00; H, 5.53.

_p_-ClC$_6$H$_4$CH(OSiMe$_3$)CCl$_2$CH=CH$_2$ (1.5099) MS, *m/e* (relative intensity) 271 (1), 235 (2), 213 (49), 128 (10), 93 (18), 75 (16), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.08 (s, 9H, -Si(CH_3)$_3$); 4.80 (s, 1H, CHCCl$_2$); 5.18 (dd, J= 10 Hz, 1Hz, 1H, HC=CHH *cis*); 5.40 (dd, J= 16 Hz, 1Hz, 1H, HC=CHH *trans*); 6.05 (dd, J= 10 Hz, 16 Hz, 1H, HC=CH$_2$); 7.20 (s, 4H, C$_6\mathit{H}_4$). Calcd for C$_{13}$H$_{17}$Cl$_3$OSi: C, 48.23; H, 5.29. Found: C, 48.70; H, 5.15.

_o_-MeOC$_6$H$_4$CH(OSiMe$_3$)CH$_2$CH=CCl$_2$ (1.5103) MS, *m/e* (relative intensity) 209 (86), 135 (15), 75 (24), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.01 (s, 9H, -Si(CH_3)$_3$); 2.45 (dd, 2H, -CH_2CH=CCl$_2$); 3.77 (s, 3H, *p*-CH_3O); 5.05 (t, J= 6Hz, 1H, -C$_6$H$_4$-CH); 5.80 (t, J= 7Hz, 1H, -CH=CCl$_2$); 6.57-7.47 (m, 4H, C$_6\mathit{H}_4$). Calcd for C$_{13}$H$_{18}$Cl$_2$O$_2$Si: C, 52.66; H, 6.31. Found: C, 52.33; H, 6.52.

_o_-MeOC$_6$H$_4$CH(OSiMe$_3$)CCl$_2$CH=CH$_2$ (1.5140) MS, *m/e* (relative intensity) 267 (1), 231 (1), 209 (96), 135 (22), 93 (18), 91 (12), 75 (18), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.04 (s, 9H, -Si(CH_3)$_3$); 3.77 (s, 3H, *p*-CH_3O); 5.13 (dd, J= 10 Hz, 1Hz, 1H, HC=CHH *cis*); 5.45 (dd, J= 16 Hz, 1Hz, 1H, HC=CHH *trans*); 5.50 (s, 1H, CHCCl$_2$); 6.12 (dd, J= 10 Hz, 16 Hz, 1H, HC=CH$_2$); 6.60-7.60 (m, 4H, C$_6\mathit{H}_4$). Calcd for C$_{14}$H$_{20}$Cl$_2$O$_2$Si: C, 52.66; H, 6.31. Found: C, 52.90; H, 6.46.

_p_-MeOC$_6$H$_4$CH(OSiMe$_3$)CH$_2$CH=CCl$_2$ (1.5123) MS, *m/e* (relative intensity) 209 (69), 135 (13), 75 (13), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.01 (s, 9H, -Si(CH_3)$_3$); 2.50 (dd, 2H, -CH_2CH=CCl$_2$); 3.75 (s, 3H, *p*-CH_3O); 4.65 (t, J= 6Hz, 1H, -C$_6$H$_4$-CH); 5.80 (t, J= 7Hz, 1H, -CH=CCl$_2$); 6.70-7.30 (m, 4H, C$_6\mathit{H}_4$).Calcd for C$_{14}$H$_{20}$Cl$_2$O$_2$Si: C, 52.66; H, 6.31. Found: C, 51.99; H, 6.05.

_p_-MeOC$_6$H$_4$CH(OSiMe$_3$)CCl$_2$CH=CH$_2$ (1.5165) MS, *m/e* (relative intensity) 267 (1), 247 (1), 231 (3), 209 (91), 135 (22), 93 (18), 75 (10), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.04 (s, 9H, -Si(CH_3)$_3$); 3.75 (s, 3H, *p*-CH_3O); 4.83 (s, 1H, CHCCl$_2$); 5.20 (dd, J= 10 Hz, 1Hz, 1H, HC=CHH *cis*); 5.47 (dd, J= 16 Hz, 1Hz, 1H, HC=CHH *trans*); 6.13 (dd, J= 10 Hz, 16 Hz, 1H, HC=CH$_2$); 6.60-7.40 (m, 4H, C$_6\mathit{H}_4$).Calcd for C$_{14}$H$_{20}$Cl$_2$O$_2$Si: C, 52.66; H, 6.31. Found: C, 52.78; H, 6.33.

o-MeC$_6$H$_4$CH(OSiMe$_3$)CH$_2$CH=CCl$_2$ (1.5030) MS, *m/e* (relative intensity) 193 (50), 91 (12), 75 (37), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.01 (s, 9H, -Si(CH_3)$_3$); 2.35 (s, 3H, o-CH_3); 2.37 (dd, 2H, -CH_2CH=CCl$_2$); 4.90 (t, J= 6Hz, 1H, -C$_6$H$_4$-CH); 5.90 (t, J= 7Hz, 1H, -CH=CCl$_2$); 6.95-7.40 (m, 4H, C$_6\mathit{H}_4$). Calcd for C$_{14}$H$_{20}$Cl$_2$OSi: C, 55.44; H, 6.65. Found: C, 55.00; H, 6.88.

o-MeC$_6$H$_4$CH(OSiMe$_3$)CCl$_2$CH=CH$_2$ (1.5100) MS, *m/e* (relative intensity) 251 (1), 215 (3), 193 (96), 128 (11), 91 (16), 93 (12), 75 (11), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.03 (s, 9H, -Si(CH_3)$_3$); 2.35 (s, 3H, o-CH_3); 5.25 (s, 1H, CHCCl$_2$); 5.30 (dd, J= 10 Hz, 1Hz, 1H, HC=CHH *cis*); 5.47 (dd, J= 16 Hz, 1Hz, 1H, HC=CHH *trans*); 6.25 (dd, J= 10 Hz, 16 Hz, 1H, HC=CH$_2$); 7.00-7.53 (m, 4H, C$_6\mathit{H}_4$).Calcd for C$_{14}$H$_{20}$Cl$_2$OSi: C, 55.44; H, 6.65. Found: C, 55.90; H, 6.75.

p-MeC$_6$H$_4$CH(OSiMe$_3$)CH$_2$CH=CCl$_2$ (1.5052) MS, *m/e* (relative intensity) 193 (85), 93 (10), 91 (16), 75 (44), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.01 (s, 9H, -Si(CH_3)$_3$); 2.30 (s, 3H, p-CH_3); 2.45 dd, 2H, -CH_2CH=CCl$_2$); 4.60 (t, J= 6Hz, 1H, -C$_6$H$_4$-CHCH$_2$); 5.78 (t, J= 7Hz, 1H, -CH=CCl$_2$); 7.08 (s, 4H, C$_6\mathit{H}_4$).Calcd for C$_{14}$H$_{20}$Cl$_2$OSi: C, 55.44; H, 6.65. Found: C, 55.78; H, 6.77.

p-MeC$_6$H$_4$CH(OSiMe$_3$)CCl$_2$CH=CH$_2$ (1.5020) MS, *m/e* (relative intensity) 251 (1), 231 (1), 215 (5), 193 (93), 128 (10), 93 (11), 91 (12), 75 (10), 73 (100); ^{1}H *n.m.r.* δ (CCl$_4$) 0.04 (s, 9H, -Si(CH_3)$_3$); 2.27 (s, 3H, p-CH_3); 4.80 (s, 1H, CHCCl$_2$); 5.17 (dd, J= 10 Hz, 1Hz, 1H, HC=CHH *cis*); 5.45 (dd, J= 16 Hz, 1Hz, 1H, HC=CHH *trans*); 6.13 (dd, J= 10 Hz, 16 Hz, 1H, HC=CH$_2$); 6.80-7.30 (m, 4H, C$_6\mathit{H}_4$).Calcd for C$_{14}$H$_{20}$Cl$_2$OSi: C, 55.44; H, 6.65. Found: C, 55.85; H, 6.40.

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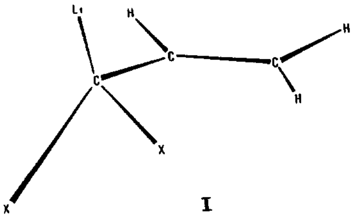

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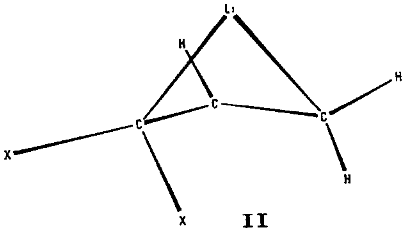

II

Among them for X=F I is the most stable structure, while for X=Cl both structures I and II exist and show almost equal stability ($\Delta E_{RHF/3-21G(*)}$=2.2 Kcal mol^{-1}).

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