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FRONTIER MOLECULAR ORBITALS OF SILYL- AND DISILANYL-PROPADIENES AND -PROPYNES AND THEIR PHOTOCHEMISTRY

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Summary

Application of Fukui-theory to the photolysis of 1-disilanyl-3-trimethylsilyl-3-phenylpropynes and 1-disilanyl-1,3-bis(trimethylsilyl)-3-phenylpropadienes offers a reasonable explanation for the [1,3]-sigmatropic shifts of disilanyl and silyl groups observed in recent photolysis experiments. The photochemical process involves internal conversion between S states of acetylenes and allenes.

Introduction

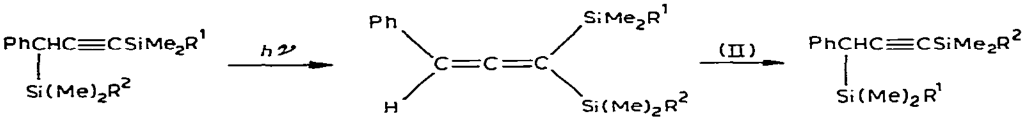
During a series of previous investigations on the photochemistry of unsaturated polysilane derivatives, formation of reactive silicon species was found to be a usual step in the reaction pathways [1—6]. However, photolysis of either 1-disilanyl-3-trimethylsilyl-3-phenylpropynes or 1-disilanyl-1,3-bis(trimethylsilyl)-3-phenylpropadienes did not give such species [4]. Both systems underwent photochemical [1,3]-isomerization and yielded an equilibrium mixture of propynes and propadienes or 1-disilanyl-1,3-bis(trimethylsilyl)- and 3-disilanyl-1,1-bis(trimethylsilyl)-propadienes. This pathway was observed irrespective of whether the solvents were protic or aprotic and of whether the substituents were electron releasing or withdrawing or bulky or small [5]. Interestingly, none of the tris(monosilyl)-3-phenylpropadienes afforded the corresponding rearranged derivative. Nevertheless, 1,3-bis(monosilyl)-3-phenylpropynes underwent a photochemical [1,3]-silylmigration (Schemes 1,2). A special feature of these photoisomerizations is that [1,3]-shift of the benzylic hydrogen to the unsaturated carbon did not occur.

Trissilylphenylpropadiene underwent thermal [1,3]-rearrangement, whereas bissilylphenylpropyne was thermally stable (Scheme 2) [6].

These observations suggest a "no-mechanism" percycyclic reaction i.e. a [3,3]- or rather two [1,3]-sigmatropic shifts of the silicons involved. Thus the photochemical reactions must be controlled by the frontier orbital interactions.

(Continued on p. 158)

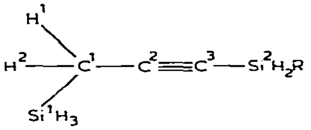
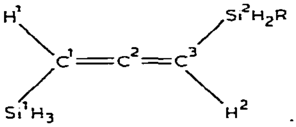
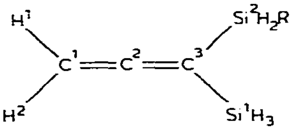
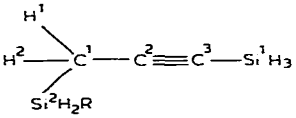
SCHEME 1



	Equilibrium mixture acetylene (%)	allene (%)
$R^1 = R^2 = Me_3Si$	13	87
$R^1 = Me_3Si, R^2 = Me$	5	95
$R^1 = Et, R^2 = Me$	3	97
$R^1 = Me_3SiCH_2, R^2 = Me$	13	87
$R^1 = Ph, R^2 = Me$	10	90

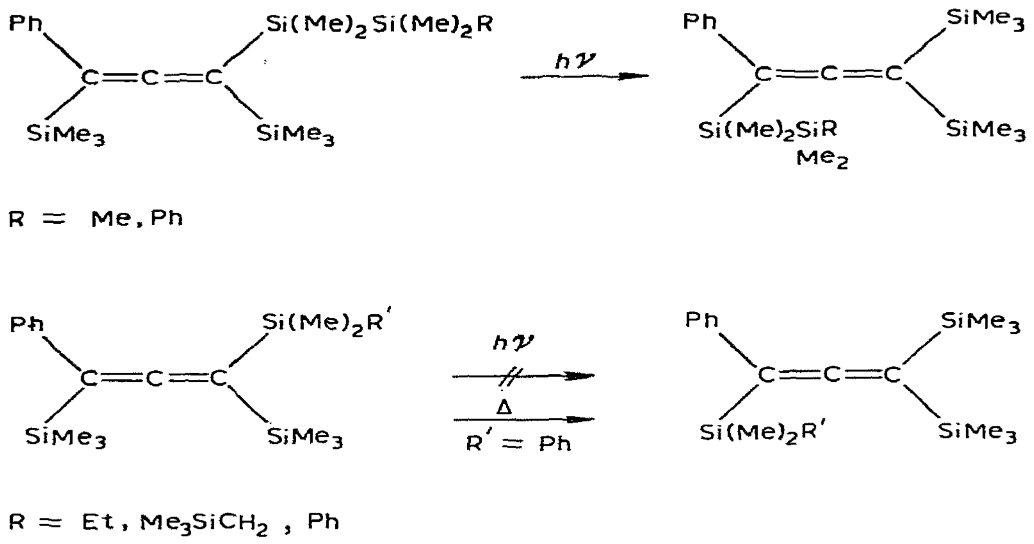
TABLE 1

CHARACTERISTIC CNDO/2 RESULTS FOR PERHYDROSILYL- AND PERHYDRODISILANYL-PROPYNES AND -PROPADIENES. DISUBSTITUTED COMPOUNDS

Structure	R	Total energy (a.u.)[a]	Energy of frontier MO (a.u.)[a]			
			HOMO	LUMO	N_1LUMO	N_2LUMO
(A) 	C^4H_3	−43.11069	−0.44	0.035	0.073	0.13
	Si^3H_3	−40.15109	−0.43	0.054	0.056	0.084
(B') 	C^4H_3	−43.09306	−0.42	0.059	0.065	0.12
	Si^3H_3					
B'^t (90°-twisted B')	C^4H_3	−42.91092	−0.31	−0.059	0.061	0.084
	Si^3H_3					
(B') 	C^4H_3	−43.10008	−0.39	0.052	0.059	0.11
	Si^3H_3	−40.13988	−0.39	0.046	0.053	0.075
B^t (90°-twisted B)	C^4H_3	−43.03666	−0.32	0.033	0.057	0.094
	Si^3H_3	−40.07466	−0.32	0.030	0.048	0.072
(C) 	C^4H_3	−43.10777	−0.44	0.061	0.067	0.13
	Si^3H_3	−40.14843	−0.43	0.048	0.068	0.078

[a] 1 a.u. = 2625.6 kJ/mol.

SCHEME 2



R = Me, Ph

R = Et, Me_3SiCH_2, Ph

	Net charge								
N_3LUMO	C^1	C^2	C^3	C^4	H^1	H^2	Si^1	Si^2	Si^3
0.13	−0.12	0.02	−0.24	−0.17	0.02	0.02	0.59	0.63	x
0.10	−0.12	0.01	−0.22	x	0.02	0.02	0.59	0.43	0.35
0.13	−0.24	0.11	−0.24	−0.18	0.04	0.04	0.60	0.61	x
0.11	−0.40	0.28	−0.45	−0.19	0.83	0.83	0.60	0.70	x
0.13	−0.19	0.12	−0.31	−0.18	0.03	0.03	0.63	0.64	x
0.096	−0.19	0.11	−0.29	x	0.03	0.04	0.63	0.44	0.35
0.12	−0.35	0.29	−0.50	−0.19	0.07	0.07	0.74	0.74	x
0.086	−0.35	0.29	−0.48	x	0.07	0.07	0.74	0.55	0.32
0.13	−0.13	0.02	−0.24	−0.18	0.02	0.02	0.62	0.60	x
0.099	−0.10	0.02	−0.24	x	0.02	0.01	0.62	0.40	0.35

To aid the interpretation of photolysis experiments CNDO/2 level calculations were carried out (see results in Tables 1—3).

Results and discussion

The following questions had to be answered.

1. Why can bis(monosilyl)propynes undergo [1,3]-photoisomerization to afford the corresponding propadienes while the tris(monosilyl)propadienes cannot?
2. Why can [1,3]-photoisomers be obtained from the photolysis of bissilyldisilanylpropadienes?
3. In the case of bissilylpropynes, why does a [1,3]-hydrogen shift from the benzylic carbon to the unsaturated carbon never occur?

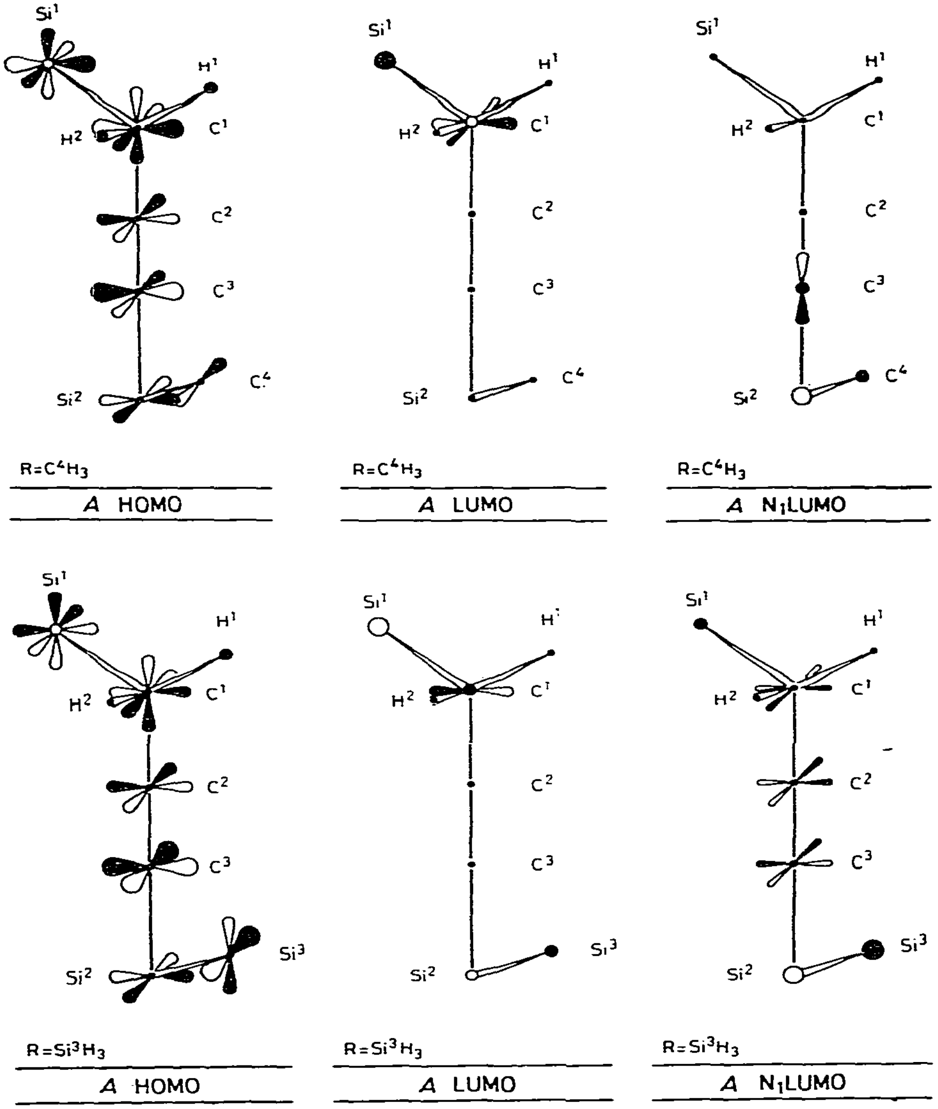
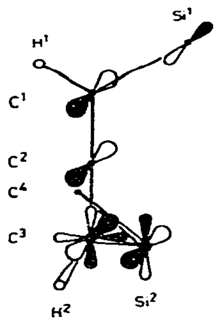
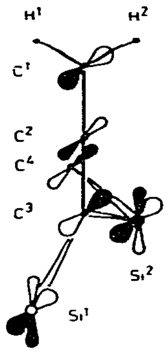


Fig. 1.



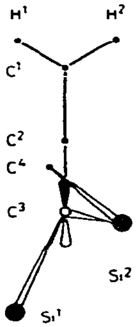
$R=C^4H_3$

B′ HOMO



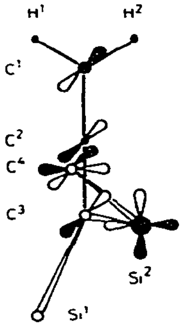
$R=C^4H_3$

B HOMO



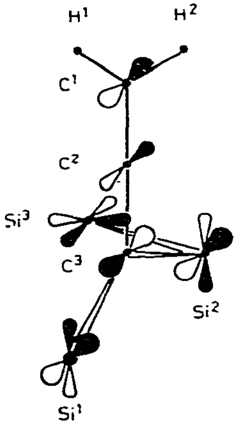
$R=C^4H_3$

B LUMO



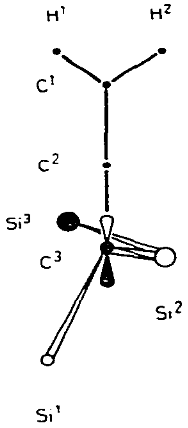
$R=C^4H_3$

B N_1LUMO



$R=Si^3H_3$

B HOMO



$R=Si^3H_3$

B LUMO

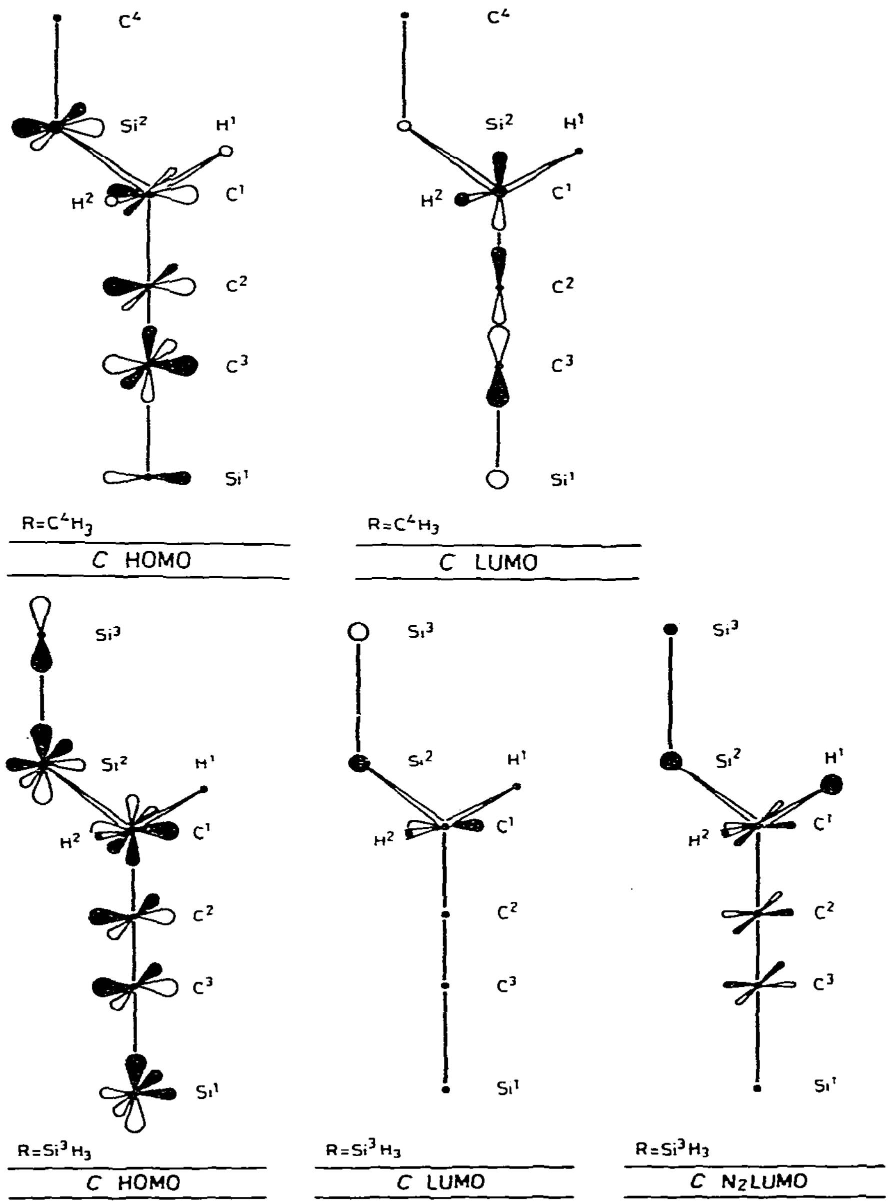


Fig. 1. Schematic representations of molecular orbitals for compounds A, B, B′ and C.

4. Why are reactive silicon intermediates not produced from disilanyl derivatives?
5. What is the general photochemical process involved, is it mixing of charge transfer configurations with ground state (LUMO—HOMO, NLUMO—HOMO), or is the favorable symmetry correlation to be found in an excited configuration (LUMO or N_iLUMO) itself?

By considering the ground state, charge-transfer and excited state configurations of the various perhydromethylsilyl-, and disilanylpropynes and -propadienes, questions 1 and 2 can plausibly be answered (Scheme 3, Table 1, Figure 1).

According to the Woodward-Hoffmann rules, a photochemical [1,3]-sigmatropic shift is allowed for a *suprafacial* mechanism, whereas [3,3] is allowed for a *supra-antara* process [9] *. Analysing the frontier MO of structures A—C, one can see, that:

i. the HOMO is the π of the unsaturated carbon-skeleton and the LUMO is the $\sigma^*(\pi^*)$ and σ^* of Si^2—C^4 or Si^2—Si^3, respectively **;
ii. there is no possibility of Si=C bond-preformation; and, furthermore;
iii. the less stable isomer B′ could have been formed only by interaction of a higher NLUMO of weak acceptor hydrogen and the HOMO of A.

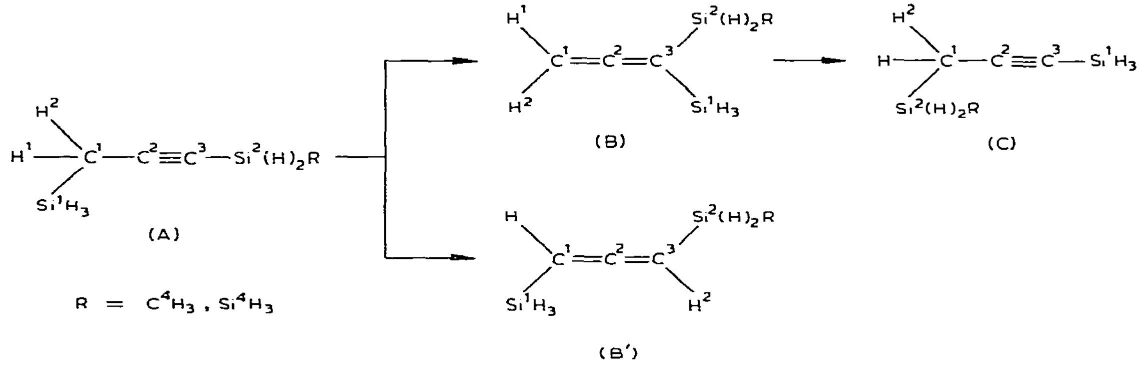
As far as *suprafacial* [1,3]-photoisomerization is concerned, process A→B can proceed via the interaction of HOMO_{C^3} and LUMO_{Si^1} when the C^1—Si^1 bond is weakened by a σ^* in the case of $R = C^4H_3$, whereas HOMO_{C^3}—$N_1\text{LUMO}_{Si^1}$ overlap can occur for $R = Si^3H_3$. A *suprafacial* [1,3]-shift of B can take place in several ways when $R = C^4H_3$. Charge-transfer in either HOMO—LUMO, HOMO—N_1-LUMO or in the excited state itself (N_1LUMO), however, C seems to be photochemically inactive. In contrast with the methylsilyl derivative, the disilanyl C with $R = Si^3H_3$ is able to form B in an equilibrium mixture characterized by Scheme 1.

Taking into account the mechanism of acetylene—allene isomerization suggested by Walsh [11], five possible intermediates can be postulated for the isomerization in Scheme 2. However, CNDO/2 calculations for the respective perhydro derivatives show an extremely high (539 kJ/mol) barrier for disilanylcyclopropene (Table 2). Similarly, the C_{2v} configuration would need 745 kJ/mol. Hence, the formation of cyclopropene and [3,3]intermediate can be ruled out. Propynes are the most probable intermediates, in the light of Scheme 4. Comparing the perhydromethylsilyl- and perhydrodisilanylpropadiene in the isomerization pathway (Scheme 4) by the method applied to process A—C, it seems obvious that

i. as far as frontier orbitals are concerned, suprafacial rearrangements E→F and/or E′→F can occur only in the case of disilanylpropadiene (Scheme 5, Figure 2);

(Continued on p. 164)

SCHEME 3



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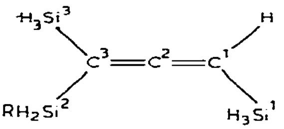
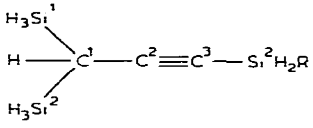
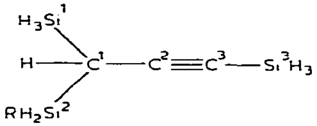
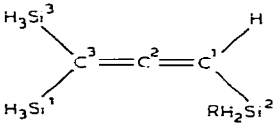
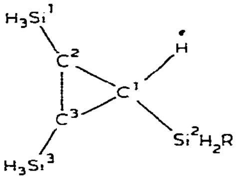
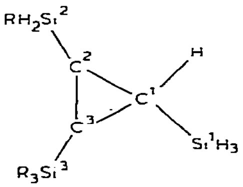
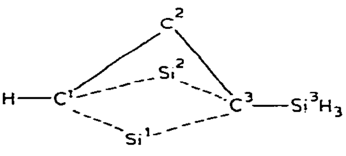
*Slutsky and Kwart carried out the pyrolysis of 3-silylpropyne at 555°C and observed the inversion of chiral silicon, i.e. the $3p$ or $3d_{z^2}$ orbital overlapped with the terminal carbon [10].

** Since the π^* of Si^2—C^4 was found to be irrelevant, schematic representations are restricted to the important σ^*.

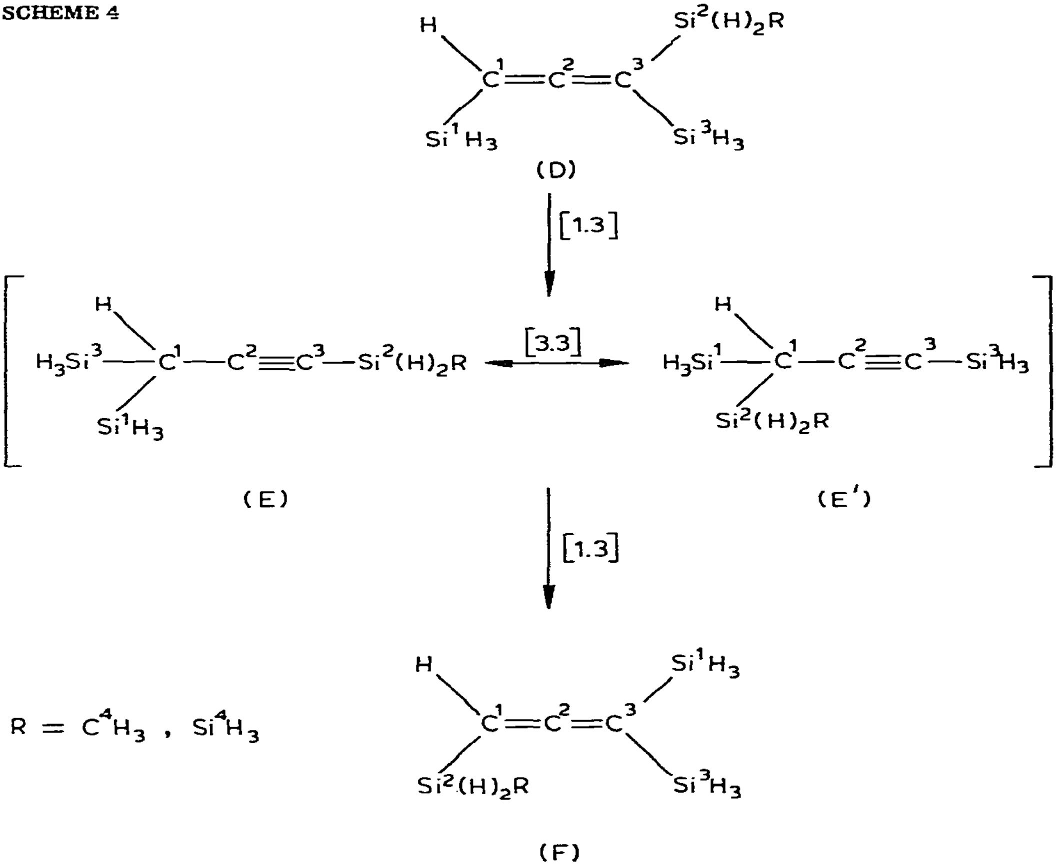
TABLE 2

CHARACTERISTIC CNDO/2 RESULTS FOR PERHYDROSILYL- AND PERHYDRODISILANYL-PROPYNES AND -PROPADIENES. TRISUBSTITUTED COMPOUNDS

Structure		Total energy (a.u.)	Energy of frontier MO (a.u.)		
			HOMO	LUMO	N_1LUMO
 (D)	R = C^4H_3	−48.37266	−0.38	0.053	0.058
	R = Si^4H_3	−45.41235	0.38	0.046	0.054
(D') (90°-twisted D)	R = C^4H_3	−48.22133	−0.31	0.048	0.060
	R = Si^4H_3	−45.25969	−0.31	0.050	0.053
 (E)	R = C^4H_3	−48.37207	−0.41	0.047	0.055
	R = Si^4H_3	−45.41244	−0.41	0.046	0.054
 (E')	R = C^4H_3	−48.36700	−0.41	0.048	0.060
	R = Si^4H_3	−45.40693	−0.41	0.044	0.048
 (F)	R = C^4H_3	−48.37127	−0.38	0.051	0.056
	R = Si^4H_3	−45.41102	−0.38	0.050	0.055
	R = C^4H_3	−48.46207			
	R = Si^4H_3	−45.50216			
	R = C^4H_3	−48.46233			
	R = Si^4H_3	−45.20700			
 3.3-intermediate triplet state	R = C^4H_3	−48.09954			
	R = Si^4H_3	−45.12953			

		Net charge						
N_2LUMO	N_3LUMO	C^1	C^2	C^3	C^4	Si^1	Si^2	Si^3
0.066	0.11	−0.28	0.14	−0.34	−0.18	0.61	0.64	x
0.062	0.077	−0.28	0.13	−0.31	x	0.61	0.45	0.35
0.066	0.083	−0.37	0.24	−0.48	−0.19	0.55	0.73	x
0.060	0.077	−0.37	0.24	−0.46	x	0.55	0.53	0.33
0.076	0.11	−0.24	0.03	−0.26	−0.18	0.62	0.62	x
0.058	0.086	−0.23	−0.02	−0.24	x	0.62	0.44	0.35
0.070	0.11	−0.24	0.03	−0.26	−0.19	0.62	0.62	x
0.071	0.075	−0.22	0.03	−0.26	x	0.62	0.42	0.34
0.067	0.11	−0.29	0.14	−0.33	−0.18	0.63	0.62	x
0.055	0.081	−0.26	0.13	−0.33	x	0.63	0.42	0.34
		0.09	−0.03	−0.18	−0.20	0.62	0.13	x
		−0.08	0.22	−0.16	x	0.63	0.43	0.31

SCHEME 4



ii. nevertheless, thermally, i.e. in an *antarafacial* ground state process, both methylsilyl- and disilanylpropadiene may rearrange, probably with inversion at the silicon center [10];

iii. the Si=C double bond can be preformed only in disilanylpropadiene in the higher N_4LUMO configuration, which is obviously not involved.

There is no way for [1,3]-photorearrangement to occur in the case of methylsilylpropadienes, whereas it is symmetry-allowed for disilanyl derivatives. Considering the total energies, the formation of a triplet state 3,3-intermediate can be ruled out. The existence of a 90°-twisted planar singlet D_{2h} allene seems probable, and so the photochemical processes have been assumed to be of the $S_0 \rightarrow S_1 \rightarrow S_0$ type. Corresponding allene-acetylene derivatives differ merely in their vibrational-rotational states (Table 3) and the intercommunication among different S-states may proceed by internal conversion.

We believe this to be the first time the Woodward-Hoffmann rules and Fukui theory have been combined to interpret the photochemistry of silyl- and disilanylallenes of C_1 symmetry, and the approach seems to provide a reasonable interpretation of the photolysis experiments. To support the conclusions presented here, detailed calculations on the ground and excited states of the title compounds are now in progress using the modified CNDO procedure of Scharfenberg [12].

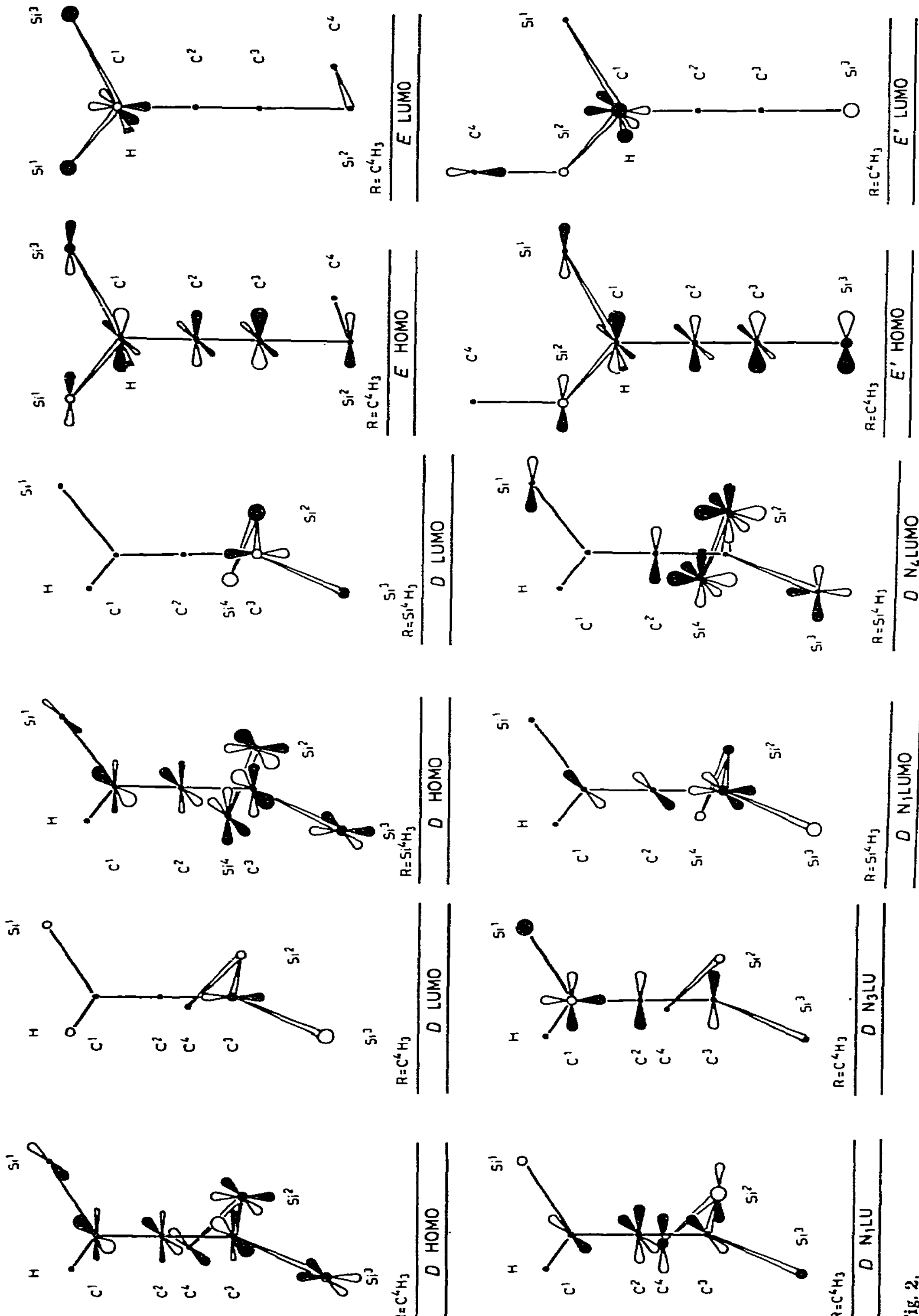
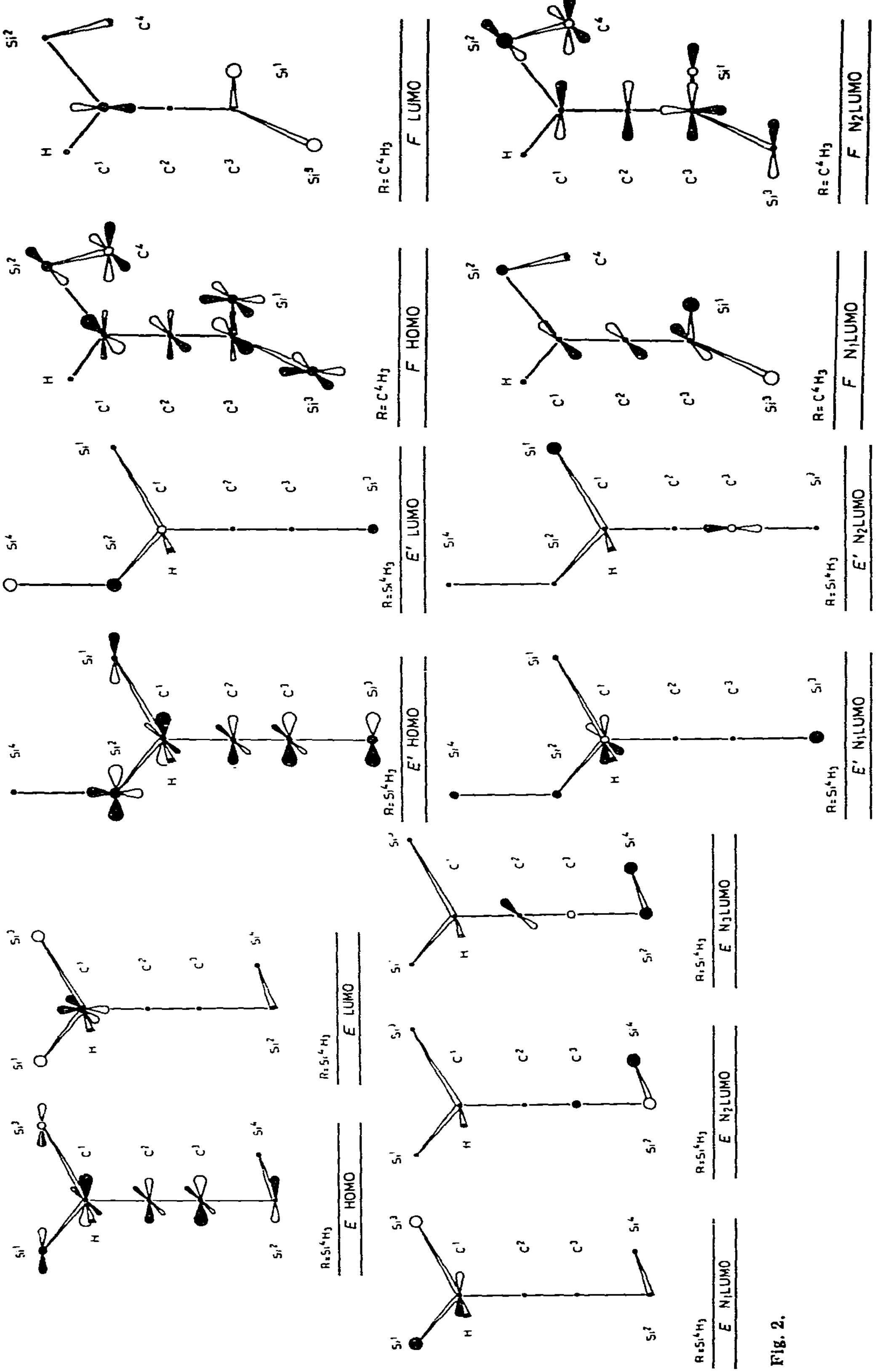

R=C4H3
D HOMO
R=C4H3
D LUMO
R=Si4H3
D HOMO
R=Si4H3
D LUMO
R=C4H3
E HOMO
R=C4H3
E LUMO
R=C4H3
D N1LU
R=C4H3
D N3LU
R=Si4H3
D N1LUMO
R=Si4H3
D N4LUMO
R=C4H3
E' HOMO
R=C4H3
E' LUMO
H
C1
C2
C3
C4
Si1
Si2
Si3
Si4

Fig. 2.



R: Si⁴H₃ E HOMO

R: Si⁴H₃ E LUMO

R: Si⁴H₃ E N₁LUMO

R: Si⁴H₃ E N₂LUMO

R: Si⁴H₃ E N₁LUMO

R: Si⁴H₃ E' HOMO

R: Si⁴H₃ E' N₁LUMO

R: Si⁴H₃ E' LUMO

R: Si⁴H₃ E' N₂LUMO

R: C⁴H₃ F HOMO

R: C⁴H₃ F N₁LUMO

R: C⁴H₃ F LUMO

R: C⁴H₃ F N₂LUMO

Fig. 2.

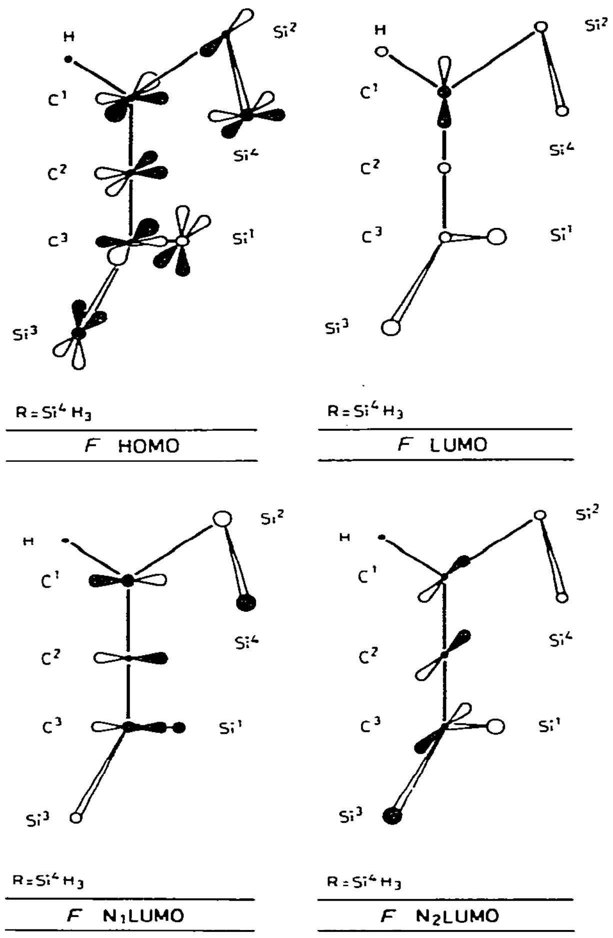


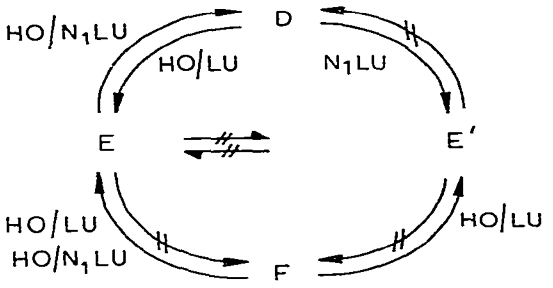
Fig. 2. Schematic representations of molecular orbitals for compounds O, E, E' and F.

Experimental

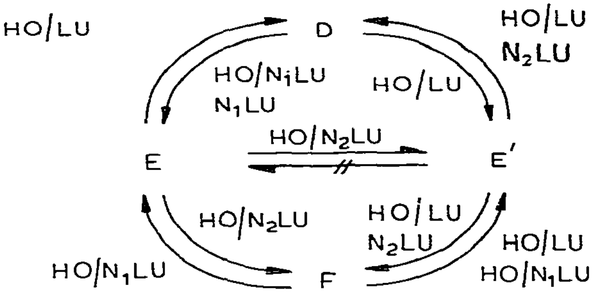
The calculations were carried out with a slightly modified version of QCPE-141 program on an ICT-1900 computer. Standard interatomic distances (pm) and bond angles (degrees) were used [7,8] (Fig. 3). All molecular structures were assumed to have the same *gauche* configuration. The geometries of C_{2v} intermediates were derived from ab initio calculations [8]. The calculations have been limited to the *sp* basis set.

SCHEME 5

HO/N_1LU, HO/LU refer to favourable overlep of HOMO—N_1LUMO, HOMO—LUMO corresponding to *suprafacial* E⇌O photoisomerization



R = C^4H_3

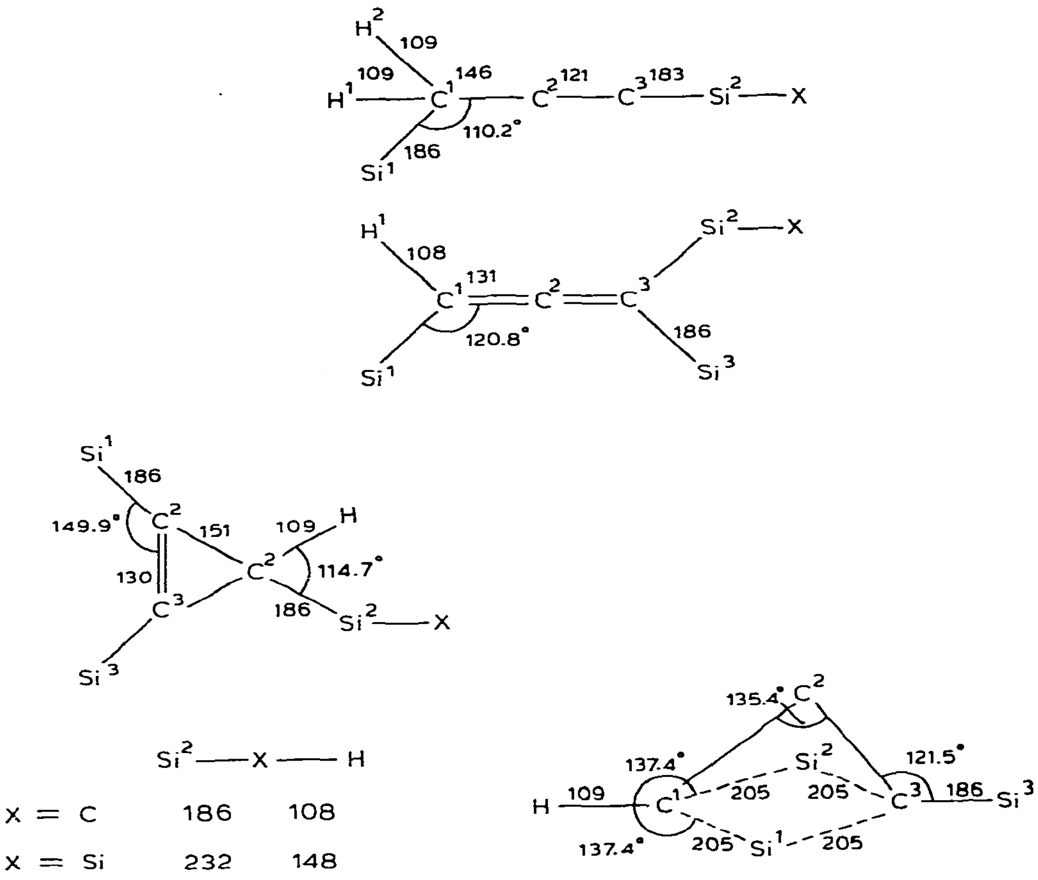


R = Si^4H_3

TABLE 3

TOTAL ENERGY OF DERIVATIVES A—F RELATIVE TO THE GROUND STATE (kJ/MOL)

Model compound	R			State	Local symmetry of C-skeleton
	C^4H_3	Si^3H_3	Si^4H_3		
A	0	0		S_{0,ac^1}	C_{3v}
B^t	194.3	200.5		$S^{v}_{1,\mathrm{al}}$	D_{2h}
B	27.03	29.31		$S_{0,\mathrm{al}}$	D_{2d}
C	7.542	6.701		S_{0,ac^2}	C_{3v}
D	0		0	S_{0,al^1}	D_{2d}
D^t	397.3		400.7	$S^{v}_{1,\mathrm{al}}$	D_{2h}
E	1.263		−0.42	$S_{0,\mathrm{ac}}$	C_{3v}
E′	14.65		14.24	$S^{v}_{0,\mathrm{ac}}$	C_{3v}
3,3-intermediate	712.2		742.3	T_1	C_{2v}
F	8.717		3.768	S_{0,al^2}	D_{2d}



	Si²—X	X—H
X = C	186	108
X = Si	232	148

Fig. 3. Bond distances and angles used in the calculations.

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