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ABSTRACT

Semiempirical and ab initio Hartree Fock computational results indicate that the highly reactive dienophile tetramethyldisilene, $Me_2Si{=}SiMe_2$, is an excellent candidate for a novel functionalization of the equator of C_{70} via a [2+4] cycloaddition to the 21, 22, 23, 42 carbons. Thermal or photochemical generation of tetramethyldisilene in the presence of C_{70} results in similar complex mixtures in which the major product appears to be that of [2+2] cycloaddition to the 7,8 carbons of C_{70}. A minor product clearly results from [2+2] cycloaddition to the 1,9 carbons. Both of these products are hydrolytically unstable and are converted nonspecifically to mixtures of 1,9- and 7,8-$C_{70}H_2$ which are also present in HPLC traces of the reaction mixtures.

INTRODUCTION

The chemistry of C_{70} has to a large measure paralleled that of C_{60}. C_{70}'s lower symmetry gives rise to several possible products, in contrast to the single product often found in additions to C_{60}. In some cases the chemo- or regioisomers can be equilibrated to yield differential free

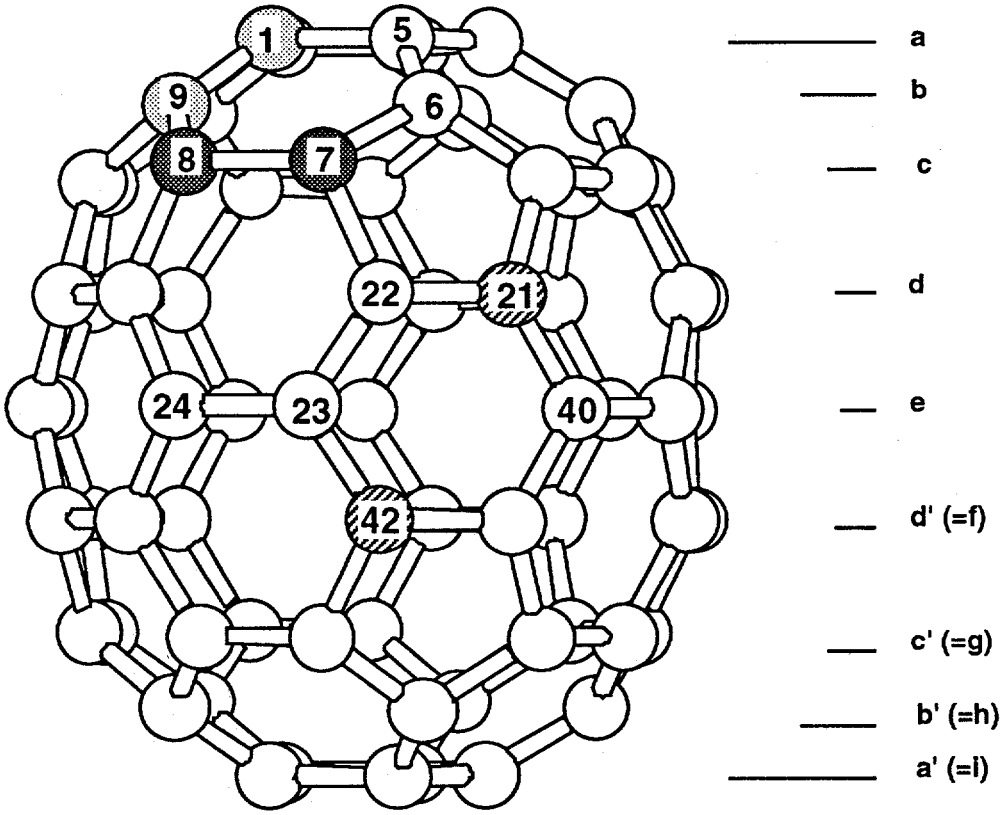


Figure 1. C_{70} nomenclature. Addition to the 21,42 positions is predicted to be favorable, but only additions to the 1,9 and 7,8 positions has so far been observed.

DISCLAIMER

energies of formation that yield insight into the fundamental chemical nature of C_{70}.[1] A unique low energy addition pattern -- addition to the 21,42 carbons of C_{70} -- was first identified by semiempirical calculations on $C_{70}H_2$ and verified by ab initio Hartree-Fock methods.[2] This addition pattern is 1,4 across a 6-ring that spans the equator of C_{70} as is shown in Figure 1. However, it is perhaps best described as addition to one carbon in each hemisphere of C_{70}.

These calculations on $C_{70}H_2$ prompted the search for methods to functionalize the equatorial region of C_{70} chemoselectively with applications to both materials and pharmaceuticals. Because the energy of the 21,42 isomer of $C_{70}H_2$ is estimated to lie 4.5 kcal/mol higher in energy than the lowest energy 1,9-isomer, [2+4] cycloadditions to C_{70} were proposed as the most direct route to functionalization of the C_{70} equatorial region. There are many examples of fullerenes reacting as the 2-atom reagent in cycloadditions; this would be the first example of a fullerene reacting as the 4-atom component.

SEMIEMPIRICAL CALCULATIONS

A series of semiempirical calculations were undertaken in order to focus the experimental program. The MNDO/PM3[3] heats of reaction of C_{70} with common dienophiles to yield 21,42-addended C_{70} [2+4] cycloaddition products are presented in Table 1. With the exception of benzyne, none of the products containing only first row atoms was significantly thermodynamically stable with respect to cycloreversion. The final geometries clearly show high

Table 1. Results of semiempirical calculations on [2+4] cycloadditions to C_{70}'s 21,42 carbons

Ene Component	ΔH_f (C_{70}) kcal/mol	ΔH_f(Ene) kcal/mol	Sum (Reagents)	Sum (Product)	$\Delta\Delta H_f$ kcal/mol
Ethylene	884.17	16.61	900.78	908.67	7.90
Acetylene	884.17	50.69	934.86	950.67	15.82
2-Butyne	884.17	29.77	913.94	930.42	16.48
Maleic anhydride	884.17	-90.08	794.09	806.55	12.46
DMAD[a]	884.17	-107.87	776.30	794.48	18.19
DEAD[b]	884.17	-128.36	755.81	794.41	38.60
HF2B[c]	884.17	-253.66	630.51	643.67	13.16
Benzyne	884.17	129.89	1014.1	954.32	-59.74
Fumaronitrile	884.17	85.99	970.16	990.69	20.53
Cyclobutene	884.17	37.67	921.84	922.41	0.57
Corrected C_4H_6[d]				933.03	12.19
Dicyanoacetylene	884.17	127.99	1012.20	1026.8	14.69
trans-1,2-$C_2H_2F_2$	884.17	-71.52	812.65	825.98	13.33
S-acetaldehyde	884.17	29.17	913.34	908.15	-5.19
cyclo-C_3F_4	884.17	-102.48	781.69	779.04	-2.65
MeOC≡COMe	884.17	-9.66	874.51	877.32	2.81
Cyclopropene	884.17	68.17	952.34	949.04	-3.30
$H_2Si=SiH_2$[e]	884.17	56.81	940.98	865.36	-75.62

[a]Dimethylacetylene dicarboxylate
[b]Diethylazo dicarboxylate
[c]Hexafluoro-2-butyne
[d]Hand corrected for relatively poor calculated value of cyclobutene vs. cyclobutane
[e]Accuracy of disilene heat of formation is not known

bond strain in the products which can be attributed to C_{70}'s rigid framework which does not accommodate the short bonds that result from the cycloaddition of dienophiles with first row elements.

In contrast, the cycloaddition of disilenes, $R_2Si{=}SiR_2$, with C_{70} is predicted to be highly exothermic. Although the exact heat of formation of the disilene may be poorly estimated by semiempirical calculations, the exothermicity of the reaction is assured. The thermodynamic stability of the product can be ascribed to two factors: the relatively high energy of the disilene dienophile and the long Si-Si bond in the final product that does not require significant conformational changes in the C_{70} framework upon cycloaddition.

A more complete analysis of cycloadditions of disilene, $H_2Si{=}SiH_2$, to C_{70} is presented in Table 2. The product of [2+2] cycloaddition of disilene to the 7,8 carbons of C_{70} is the lowest energy isomer at a semiempirical level; however, other products of [2+2] and [2+4] addition are only slightly higher in energy.

Table 2. Heats of reaction (MNDO/PM3) and relative energies of isomers (HF/3-21G*) of Si_2H_4 with C_{70}. All geometries fully optimized, energies in kcal/mol.

Addended Carbons	Cycloaddition	ΔH_f (PM3) kcal/mol	$\Delta\Delta H_f$ kcal/mol[a]	Relative ΔE HF/3-21G*	R(Si-Si) Å HF/3-21G*
23,40	[2 + 4]	911.75	-29.23		
8,23	[2 + 4]	888.19	-52.79		
6,9	[2 + 4]	882.13	-58.85		
21,40	[2 + 2]	879.99	-60.99		
1,7	[2 + 4]	878.14	-62.84		
21,22	[2 + 2]	869.28	-71.70	10.6	2.322
21,42	[2 + 4]	865.36	-75.62	0	2.402
1,9	[2 + 2]	863.31	-77.67	3.3	2.322
7,8	[2 + 2]	862.24	-78.74	4.1	2.322

[a]Based on $\Delta H_f(C_{70})$ = 884.17 and $\Delta H_f(Si_2H_4)$ = 56.81 kcal/mol.

AB INITIO-HARTREE FOCK CALCULATIONS

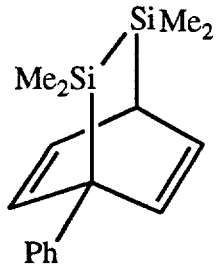
The four lowest energy isomers of $C_{70}Si_2H_4$ were then chosen as candidates for further investigation using ab initio methods with the GAUSSIAN 92 series of programs.[5] For computational convenience, the methyl groups (used in the experimental work, see below) were replaced by hydrogens. Complete geometry optimizations were performed at the Hartree-Fock (HF) level using the 3-21G* basis set, which contains one set of spherical harmonic d functions on each silicon. A summary of the ab initio results is given in Table 2.

These calculations indicate that the most stable product from cycloaddition of a disilene with C_{70} is that from [2+4] addition across the C_{70} equator. Semiempirical and ab initio calculations suggest different energy orderings; however, semiempirical calculations are known to be less reliable in predicting isomer energy orderings in fullerenes.[1,4] Therefore, the thermodynamically most stable product from disilene addition is predicted be the 21,42-isomer.

Interestingly, the Si-Si bond lengths in the other three isomers are identical and shorter than the Si-Si bond length in the 21,42 product, and similar to the unstrained HF/3-21G* optimized bond length of 2.320 Å in eclipsed Si_2H_6. The longer Si-Si bond in the 21,42 isomer is also consistent with the structural rigidity of the C_{70} framework. The [2+2] products may lie higher in energy due angle strain in the four-membered C_2Si_2 rings.

RESULTS AND DISCUSSION

Although a facile route to disilene, Si_2H_4, is not available, tetramethyldisilene can be generated from thermolysis or photolysis of its biphenyl adduct, 2,3-disila-1-phenyl-2,2,3,3-tetramethyl-



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bicyclo[2.2.2]octa-5,7-diene, **1**.[6,7] Both thermal and photochemical reactions of **1** with C_{70} yield similar product distributions, and, together with previous reports of the thermal chemistry of **1**, strongly support intermediacy of tetramethyldisilene.

The photochemical reaction proceeds with either 254 or 366 nm light, but **1** is transparent to 366 nm light. Based on accepted mechanisms of redox interactions between fullerenes and silanes, formation of either a charge-transfer stabilized exciplex or a radical ion pair can explain the formation of tetramethyldisilene in the photochemical case.

HPLC analysis (Figure 2) shows that several fullerene-derived products are formed in the reaction. In laboratory atmosphere and lighting, the products slowly convert to the hydrogenated fullerenes 1,9- and 7,8-$C_{70}H_2$, which have been identified by comparison of HPLC retention times and UV-Vis spectra of authentic samples. Hydrogenated fullerenes are rapidly produced by treatment of either reaction mixtures or solutions of purified silicon-containing products with triflic acid.

Comparison of UV spectra of $C_{70}H_2$ isomers with those of the two new compounds t_R=11.16 and t_R=11.80 isolated from the reaction provides compelling, but not unequivocal, evidence for structural assignments. By inspection, we assign the major product as that of 7,8-addition and the minor product as the result of 1,9-attachment to the fullerene cage.

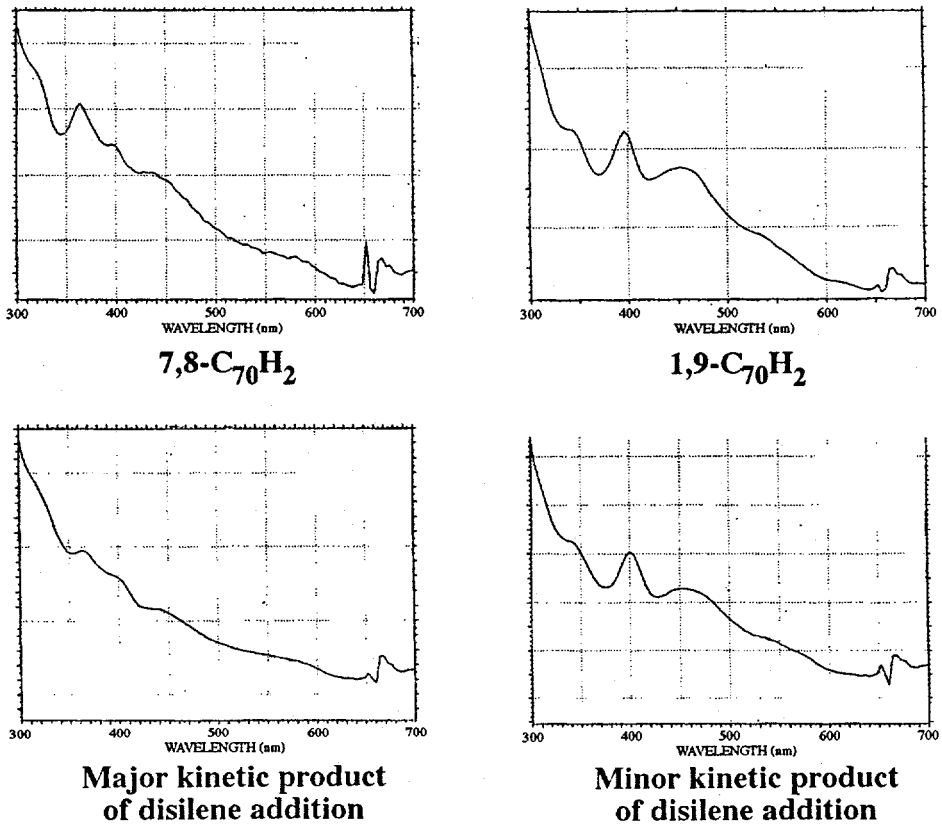


Figure 2. Photodiode array UV/Vis spectra of the $C_{70}H_2$ isomers and products of disilene addition.

In addition to the diagnostic UV-Vis spectral agreement, peaks due to silicon-bound methyl groups are apparent in the ^{1}H NMR spectra of reaction mixtures. The starred peaks (Figure 4) are due to the starting material, **1**. Sufficient pure material for spectral characterization of the disilene adducts is not yet available.

EXPERIMENTAL

Thermal reaction. A solution of 2,3-disila-1-phenyl-2,2,3,3-tetramethylbicyclo[2.2.2]octa-5,7-diene (10 mg) and C_{70} (4 mg) in toluene (6 ml) was placed in a Teflon-valve-sealed glass reaction tube (KONTES 218710-0050) and subjected to three freeze-pump-thaw degassing cycles. The mixture was heated in a 265 °C sand bath for 9 hours. HPLC analysis of the reaction mixture (Figure 3(a); 4.6 x 250 mm Buckyclutcher I column, 3:2 toluene:hexane mobile phase, 2.25 ml/min flow rate) revealed 30% consumption of C_{70} and a product distribution similar to that obtained by photolysis. A precipitate was not obtained.

Photochemical reaction. A solution of 2,3-disila-1-phenyl-2,2,3,3-tetramethylbicyclo[2.2.2]octa-5,7-diene, **1**, (26 mg) and C_{70} (9 mg) in toluene (10 ml) was placed in a Teflon-valve-sealed glass reaction tube (KONTES 218710-0050) and subjected to three freeze-pump-thaw degassing cycles. The mixture was irradiated in a Rayonet photochemical reactor (254 nm) for 2.5 hours. HPLC analysis of the reaction mixture (Figure 3(b); 4.6 x 250 mm Buckyclutcher I column, 3:2 toluene:hexane mobile phase, 2.25 ml/min flow rate) revealed 90% consumption of C_{70} and formation of several products. Products were isolated by preparative HPLC (10 mm x 250 mm Buckyclutcher I column, 3:2 toluene:hexane mobile phase, 4.5 ml/min flow rate). With 366 nm radiation, the reaction proceeds at a lower rate, but gives a similar product distribution.

Reaction product aging. After one week with normal exposure to room light and laboratory atmosphere, HPLC analysis (Figure 3(c); 4.6 x 250 mm Buckyclutcher I column, 3:2 toluene:hexane mobile phase, 2.25 ml/min flow rate) showed the product mixtures had changed significantly . By comparison with authentic samples (retention time and UV-Vis spectra), the compounds present were identified as C_{70}, 1,9-$C_{70}H_2$, and 7,8-$C_{70}H_2$.

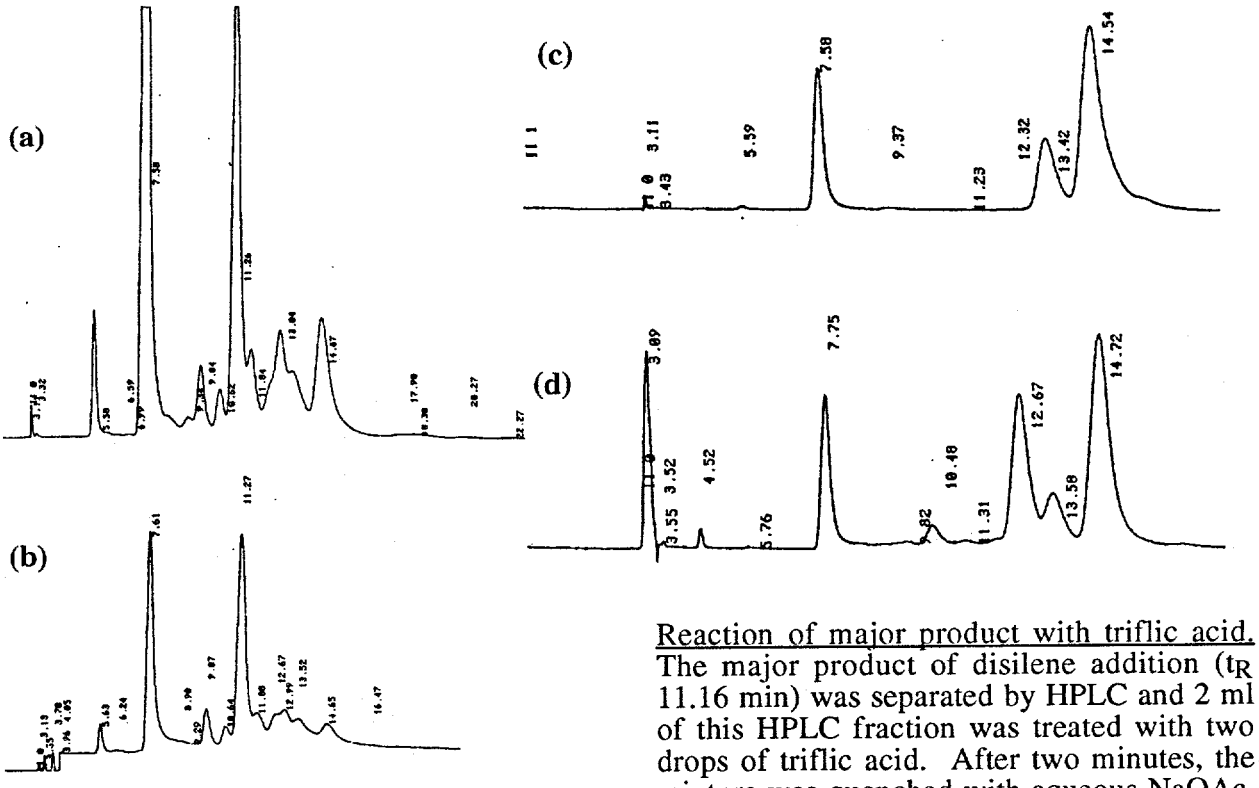
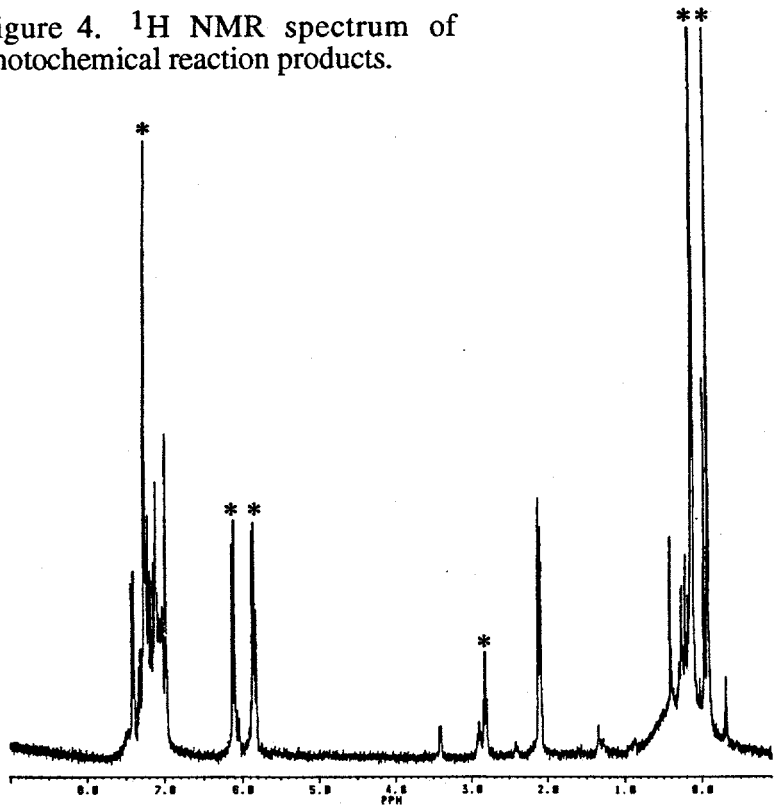


Figure 3. HPLC analyses.

Reaction of major product with triflic acid. The major product of disilene addition (t_R 11.16 min) was separated by HPLC and 2 ml of this HPLC fraction was treated with two drops of triflic acid. After two minutes, the mixture was quenched with aqueous NaOAc. HPLC analysis of this sample (Figure 3(d); 10 mm x 250 mm Buckyclutcher I column, 3:2 toluene:hexane mobile phase, 4.5 ml/min flow rate) showed complete disappearance of the disilene adduct. Three of the four products of reaction with triflic acid were identified as C_{70}, 1,9- and 7,8-$C_{70}H_2$. A new compound (t_R=12.67 min, cf. Figure 3(c)) is also present, but disappears upon standing.

Figure 4. ^1H NMR spectrum of photochemical reaction products.



CONCLUSIONS

Ab initio Hartree-Fock calculations suggest that the lowest energy product of a disilene with C_{70} is that resulting from [2+4] cycloaddition to yield a 21,42-addended product. The major product resulting from either photochemical or thermal decomposition of **1** in the presence of C_{70} is best interpreted as that from reaction at the 7,8 carbons, though reaction at the 21,42 carbons cannot be ruled out. This result is consistent with the high reactivity and high electron density of the 7,8 bond. Evidence for additions to or across the equator of C_{70} is not yet unequivocal.[8] The present results highlight the importance of kinetic considerations in functionalizations of the equator of C_{70}.

ACKNOWLEDGMENTS

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