Pergamon

Tetrahedron, Vol. 52, No. 14, pp. 4983-4994, 1996
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0040-4020/96 $15.00 + 0.00

S0040-4020(96)00106-8

An Efficient Functionalization of [60]Fullerene. Diels-Alder Reaction Using 1,3-Butadienes Substituted with Electron-Withdrawing and Electron-Donating (Silyloxy) Groups

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Abstract: The Diels-Alder strategy was found suitable for the functionalization of C_{60} using 1,3-butadienes substituted with an electron-withdrawing group as well as with an electron-donating group, giving cyclohexene-fused C_{60} derivatives having ethoxycarbonyl, acetyl, cyano, phenylsulfonyl and nitro substituents. These cycloadducts were stabilized by conjugation with the substituent and no cycloreversion took place. Though the dienes are electron-deficient in nature, the HOMO (diene) - LUMO (C_{60}) interaction was significant as indicated by PM3 calculations.

Cycloaddition reactions are the most reliable methods for functionalization of [60]fullerene because (i) the-low lying LUMO level of C_{60} is advantageous for this type of cyclization (*e.g.*, C_{60} is demonstrated to have nearly the same reactivity as *N*-phenylmaleimide[1]), (ii) the addition occurs selectively at the 6,6-ring junction with a few exceptions[2], and (iii) the number of the addends (*i.e.*, monoadduct *vs* polyadduct) is controlled with relative ease if excess amount of reagent is avoided. Therefore, a variety of [m+n]cycloaddition reactions have successfully been carried out ranging from m=1 to m=4 with C_{60} being the 2π component.[3] The pioneer work for these reactions was done by Wudl *et al.*, who first showed the remarkable Diels-Alder reactivity with cyclopentadiene and anthracene.[4] Thereafter, the cycloaddition reaction with these dienes was extensively studied.[5] The cumulative results revealed that C_{60} was reactive enough to give the corresponding 1:1 cycloadduct, but it underwent cycloreversion to the starting materials. Stability of the Diels-Alder cycloadducts was attained by incorporating the forming double bond into an aromatic ring[6]; with this aim, *o*-quinodimethanes were efficiently utilized as dienes to afford tetrahydronaphtho-fused C_{60} derivatives bearing interesting functionalities on the benzene ring.[7] Alternatively, the cycloreversion could be avoided simply by smooth conversion of the formed double bond to a single bond, as was demonstrated in the case of 2-silyloxy-1,3-dienes.[1,8] The reactivity of these dienes is electronically favorable because of their high HOMO level. Thus, this process constitutes an effective method for the introduction of a carbonyl function on the C_{60} surface. Although the results for 2-trimethylsilyloxy-1,3-butadiene (**1a**) and Danishefsky's diene (**1b**) have already been reported by Rubin and Wilson, respectively, we independently undertook the reaction of a series of silyloxydienes, and therefore, our own findings are first noted briefly. The major part of this report focusses on the reaction of C_{60} with 1,3-butadienes bearing an electron-withdrawing substituent.

RESULTS AND DISCUSSION

The Diels-Alder reaction of the parent and substituted 2-silyloxy-1,3-dienes **1a-e** was carried out by heating a toluene solution of C_{60} with 1.5 equiv. of the diene under a nitrogen atmosphere. The reaction mixture was then treated with 1 *N* HCl in THF, and chromatographed on a silica gel column to give the 1:1 cycloadducts **2a-e** after elution of unreacted C_{60}. The results are summarized in Scheme 1 and Table 1. All of the products had a strong IR absorption band around 1720 cm^{-1} (C=O), a weak but characteristic UV/vis absorption band at 432-434 nm, and a molecular ion peak in the MS expected for the 1:1 cycloadduct. The ^{1}H-NMR spectra of **2a,b** was consistent with those reported by Rubin and Wilson,[1,8] and those of the new cycloadducts **2c-e** were compatible with the assigned structure. The ^{13}C-NMR spectra had the expected signals due to C_{60} and cyclohexanone ring carbons. During a preliminary experiment using a commercially available mixture of C_{60} and C_{70} (*ca.* 4:1) with **1b**, we found that C_{70} reacted faster than C_{60}. This was clearly indicated by HPLC monitoring of the differential consumption rate of a 1:1 mixture of the fullerenes (Fig. 1). This fact suggests that C_{70} is more reactive than C_{60} in the Diels-Alder reaction, which might be explained as a result of the lower LUMO level of C_{70} over that of C_{60}.[9] Here it is worthy to note that the inverse reactivity between them was observed in the radical addition reaction.[10] The carbonyl function introduced on the C_{60} surface is useful for further conversion[8]; in our hands, **2a** was converted to the hydroxy ester **4** by a Lewis acid-catalyzed addition reaction with silyl ketene acetal **3** (vice reaction).

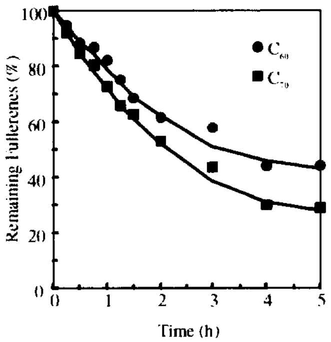
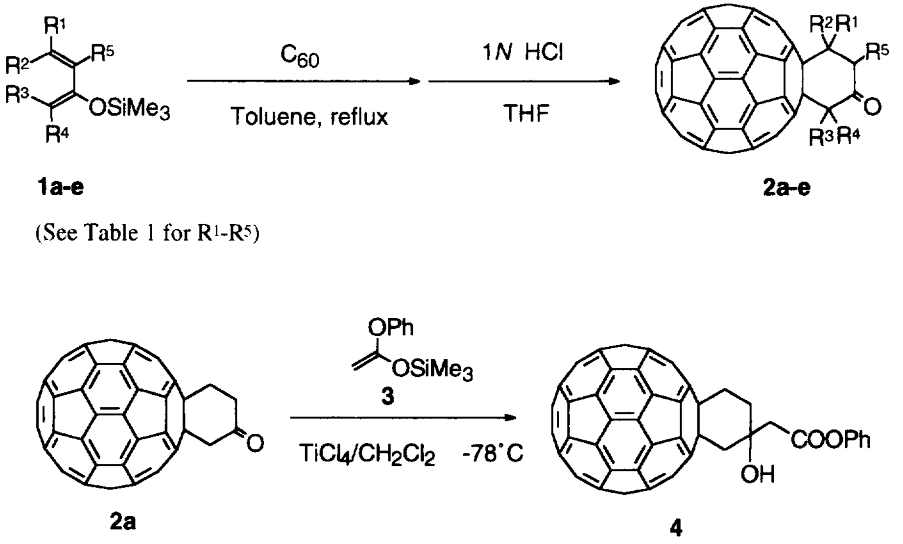


Fig. 1 Plot of the remaining fullerenes *vs.* time, for the reaction of a 1/1 mixture of C_{60}/C_{70} with **1b** at 60°C.



(See Table 1 for R^1-R^5)

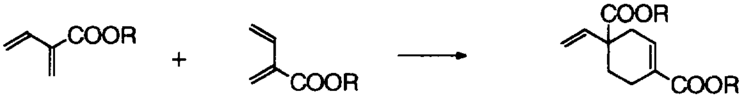
Scheme 1

Table 1. Diels-Alder reaction of C_{60} with the 2-silyloxy-1,3-dienes **2a-e**.

Diene	R^1	R^2	R^3	R^4	R^5	Temp.	Time (h)	Product	Yield[a] [recovered C_{60}]
1a	H	H	H	H	H	110°C	8	**2a**[b]	48% [15%]
1b	OMe	H	H	H	H	110°C	0.5	**2b**[b]	35% [10%]
1c	Ph	H	H	H	H	50°C	5	**2c**	29% [0%]
1d	Me	Me	H	H	H	110°C	24	**2d**	30% [10%]
1e	H	$-CH_2CH_2-$		H	H	80°C	3	**2e**[c]	47% [32%]

[a] Yields are based on consumed C_{60}. [b] The spectral data (FAB-MS, IR, ^{1}H-NMR) were consistent with those reported (ref. 1 and ref. 8). [c] This was prepared very recently by alternative methods (ref. 11).

Since C_{60} has a low LUMO level, an electron-rich diene is generally considered to be appropriate as a Diels-Alder reaction partner as mentioned above.[1,8] On the other hand, a diene having an electron-withdrawing group would seem at first to be useful if an inverse type of Diels-Alder reaction is operative, or otherwise the LUMO level of C_{60} is sufficiently low to interact with the HOMO of the electron-deficient diene. For example, it is known that 2-alkoxycarbonyl-substituted 1,3-butadienes tend to dimerize through a [4+2] cycloaddition (Scheme 2).[12,13] This fact implies that an electron-deficient olefin serves as a dienophile to such a type of diene, and possibly C_{60} does so too. From the synthetic point of view, this provides a simple method for introducing an ester group on fullerenes.



Scheme 2

We therefore started by examining the reaction of C_{60} with ethyl 2-methylene-3-butenoate (**6**)[13] (Scheme 3). The precursor of **6**, ethyl 3-hydroxy-2-methylenebutanoate (**5**), was prepared from ethyl acrylate and acetaldehyde by the Baylis-Hillman reaction,[14] for which aqueous conditions were recommended recently as an effective procedure.[15] Treatment of ester **5** with methanesulfonyl chloride/triethylamine at 0°C for 1 h and at ambient temperature for 4 h gave a dimer of the diene in 74% yield as reported previously.[13] Assuming that the dimerization is an equilibrium process, we anticipated to produce the monomer **6** at higher temperature. Thus, C_{60} was heated to reflux in *o*-dichlorobenzene in the presence of the dimer; however, no product was obtained. Therefore, the elimination reaction of ester **5** was conducted at 150°C in the presence of C_{60}, which was allowed to react with diene **6** *in situ*. In this case the color of the solution changed from purple to dark brown, and TLC analysis showed a new product (R_f=0.3, hexane/toluene 1/1). This product was separated by silica gel chromatography with hexane/toluene(1/1) elution. After recovery of C_{60} as the first fraction, cycloadduct **7** was obtained in 68% yield based on consumed C_{60}. The structure was supported by FAB-MS which had the expected molecular ion peak at m/z 846 together with a base peak at m/z 720. The IR spectrum indicated the presence of an enoate moiety at 1638 and 1709 cm^{-1}. The characteristic absorption for a 1:1 cycloadduct of C_{60} was observed at 527 cm^{-1} (IR) and 432 nm (UV/vis).[16] The ^{1}H-NMR spectrum indicated signals due to a cyclohexene ring at δ 4.20 (d, *J*=5.5 Hz, 2 H), 4.38 (s, 2 H) and 8.06 (t, *J*=5.5 Hz, 1 H); the middle singlet signal revealed that the addition occurred at the 6,6-ring junction as usual and cyclohexene ring-flipping was not restricted at room temperature. This C_s-symmetrical nature was confirmed by the ^{13}C-NMR spectrum, which indicated 30 lines due to sp^2-hybridized C_{60} ring carbons at δ 128.47-156.80 and 2 lines due to sp^3-hybridized junction carbons at δ 65.43 and 65.98 together with 3 lines due to enoate carbons at δ 165.60 and between δ 128.47-156.80.

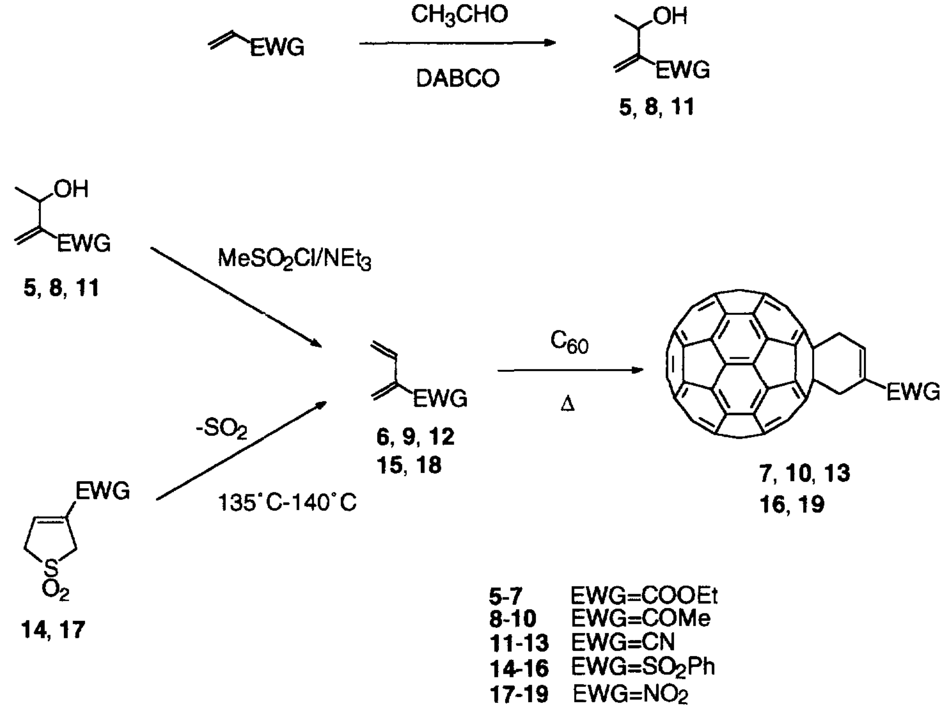
Interestingly, the cycloadduct was found to be so stable that there was no fragmentation of the C_{60}, when stored over a month. The obtained stability is attributed to conjugation of a cyclohexene double bond with a carbonyl group. Thus, stabilization of the Diels-Alder cycloadduct of C_{60} is achieved by conjugation with a substituent as well as by aromatization.[6,7] Attempts to saturate this bond by catalytic hydrogenation or reduction with Et_3SiH/CF_3COOH failed, however.

Next examined was the reaction with acetyl-substituted 1,3-butadiene following the same procedure as above. The precursor of **9**, 4-hydroxy-3-methylenepentan-2-one (**8**), was prepared similarly from methyl vinyl ketone and acetaldehyde[14] and allowed to react with methanesulfonyl chloride/triethylamine at 150°C for 30 min in the presence of C_{60}. The product arising from 3-methylene-4-penten-2-one (**9**) was chromatographed on a silica gel column to give the expected 1:1 cycloadduct **10** in 50% yield (based on consumed C_{60}) (Scheme 3). The structure was deduced in a similar way: FAB-MS m/z 816 (M$^+$), 720 (base peak); IR 1672, 1630 (enone), 527 (C_{60}) cm^{-1}; UV/vis 432 nm; ^{1}H-NMR δ 4.24 (d, *J*=5.5 Hz, 2 H), 4.32 (br s, 2 H) and 7.91 (t, *J*=5.5 Hz, 1 H); ^{13}C-NMR δ 65.09, 65.46 (junction carbons), 135.31-156.37 (all sp^2 carbons, 32 lines), and 194.43 (C=O). These data were close to the ester-substituted case and again compatible with the C_s-symmetrical 6,6-addition product.

The reaction was further extended to cyano-substituted 1,3-butadiene. Likewise, 3-hydroxy-2-methylenebutanenitrile (**11**) obtainable from acrylonitrile and acetaldehyde[14] underwent elimination reaction to 2-methylene-3-butenenitrile (**12**), which cycloadded to C_{60} to give a cyano-substituted cyclohexene-fused C_{60} derivative **13** in 49% yield (based on consumed C_{60}) (Scheme 3). The structure was primarily determined by FAB-MS [m/z 799 (M$^+$), 720 (base)], IR [2220 (CN), 1624 (C=C) and 527 cm^{-1} (C_{60})], and UV/vis (431 nm). C_s-symmetry was confirmed by ^{1}H-NMR signals at δ 4.21 (d, *J*=6 Hz, 2 H), 4.24 (s, 2 H) and 7.79 (t, *J*=6 Hz, 1 H) and ^{13}C-NMR signals at δ 64.68, 64.89 (junction carbons), 117.17 (CN) and 135.60-155.22 (all sp^2 carbons, 32 lines).

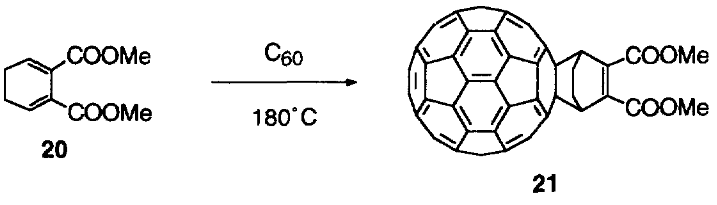
Along these lines, thermal extrusion of SO_2 from 3-sulfolene[17] was employed for the formation of a phenylsulfonyl-substituted 1,3-butadiene. Thus, 3-(phenylsulfonyl)-3-sulfolene (**14**) which was prepared by an established procedure[18] was heated in chlorobenzene at 135°C for 30 min in the presence of C_{60}. In this case change in color of the solution from purple to dark brown was also observed. The 1:1 cycloadduct **16** with 2-(phenylsulfonyl)-1,3-butadiene (**15**) formed *in situ* was isolated in 79% yield (based on consumed C_{60}) after silica gel column chromatography (Scheme 3). The structure was characterized by spectroscopic comparison with the previous data; FAB-MS m/z 914 (M$^+$), 720 (base peak); IR 1153, 1319 (SO_2), 527 (C_{60}) cm^{-1}; UV/vis 432 nm; ^{1}H-NMR δ 4.22 (d, *J*=6 Hz, 2 H), 4.28 (s, 2 H) and 7.47 (t, *J*=6 Hz, 1 H); ^{13}C-NMR δ 64.64, 65.15 (junction carbons) and 128.98-155.44 (31 lines of all the expected 36 sp^2 carbons).

Similarly, the above method was applied to the case of a nitro substituent. The required precursor 3-nitrosulfolene (**17**) was prepared from 3-sulfolene and N_2O_4 according to the reported procedure.[19] Thus, in the same manner as for the formation of **16**, C_{60} was allowed to react with 2-nitro-1,3-butadiene (**18**) *in situ* to give the nitro-substituted cycloadduct **19** in 36% yield (based on consumed C_{60}) (Scheme 3). The spectral inspection determined the structure; FAB-MS m/z 819 (M^+), 720 (base peak); IR 1522, 1335 (NO_2), 527 (C_{60}) cm^{-1}; UV/vis 431 nm; ^{1}H-NMR δ 4.31 (d, *J*=6 Hz, 2 H), 4.69 (s, 2 H) and 8.19 (t, *J*=6 Hz, 1 H); ^{13}C-NMR δ 64.73, 65.59 (junction carbons) and 134.59-155.06 (31 lines of all the expected 32 sp^2 carbons).



Scheme 3

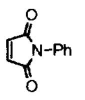
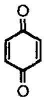
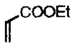
With these results in mind, we achieved bis-functionalization leading to a diester derivative by the reaction with dimethyl 2,6-cyclohexadiene-1,2-dicarboxylate (**20**) (Scheme 4). The diene in this case was isolable[20] and thus a mixture of **20** and C_{60} was heated to reflux in *o*-dichlorobenzene. After chromatographic separation, the expected cycloadduct **21** was obtained and characterized by spectral data as follows; FAB-MS m/z 916 (M^+), 720 (base peak); IR 1723, 1640 (enoate) and 527 (C_{60}) cm^{-1}; UV/vis 432 nm; ^{1}H-NMR δ 2.37 (m, 1 H), 3.28 (m, 1 H) and 4.59 (s, 1 H); ^{13}C-NMR δ 69.19 (junction carbon), 136.26-165.93 (all sp^2 carbons, 32 lines based on C_s symmetry) and 198.96 (C=O).

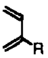


Scheme 4

From these reactions, it is obvious that C_{60} is capable of cycloadding to 1,3-butadienes substituted with an electron-withdrawing group. We calculated the HOMO and LUMO levels using PM3 for the reactants employed in the above experiment and some reference compounds. The results are summarized in Table 2. Further, the HOMO-LUMO correlation diagram between C_{60} and representative dienes is shown in Fig. 2. As expected, the LUMO of C_{60} is much lower in energy than those of typical dienophiles such as *N*-phenylmaleimide, benzoquinone and ethyl acrylate, and yet the HOMO of C_{60} is high relative to those of ethylene and butadiene. On the other hand, 1,3-butadienes with an electron-withdrawing group have a low-energy LUMO and HOMO in comparison with those with an electron-donating group. Judging from Fig. 2, the HOMO (diene) - LUMO (C_{60}) interaction dominates the cycloaddition with 2-methoxy-1,3-butadiene. This is also true for the cycloaddition with 2-ethoxycarbonyl-1,3-butadiene (**6**), since the LUMO level of C_{60} is still sufficiently low to interact with the HOMO of this diene. Thus, if anything, the inverse type of Diels-Alder reaction seems to be much less operative for the reaction of C_{60} with the electron-deficient dienes.

Table 2. The HOMO and LUMO levels of C_{60} and selected 1,3-butadienes and dienophiles (eV).

Dienophile	C_{60}	Ethylene			
LUMO	-2.888	1.228	-1.195	-1.708	-0.079
HOMO	-9.481	-10.643	-9.842	-10.920	-11.036



Diene (R)	H	OMe	COOEt	CN	COMe	SO_2Ph	NO_2
LUMO	0.281	0.224	-0.376	-0.561	-0.403	-0.515	-1.110
HOMO	-9.500	-9.090	-9.821	-10.001	-9.764	-10.083	-10.462

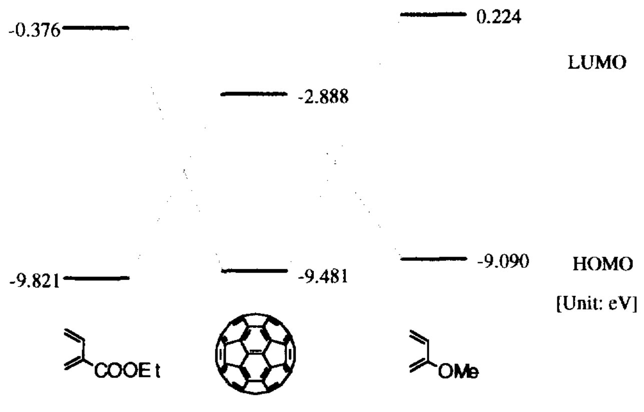


Fig. 2 Orbital interaction between C_{60} and 2-ethoxycarbonyl- and 2-methoxy-1,3-butadienes.

In summary, the described Diels-Alder reaction of C_{60} with 1,3-butadienes having an electron-donating substituent or even an electron-withdrawing substituent provides an efficient method for the introduction of diverse functionalities such as ester, ketone, nitrile, sulfone and nitro groups on the C_{60} surface. Due to the sufficiently low-energy LUMO of C_{60}, orbital interaction between HOMO (diene) - LUMO (C_{60}) is significant in the reaction with electron-withdrawing group substituted 1,3-butadienes as with 2-silyloxy-1,3-butadiene. The obtained cycloadduct is stable enough for isolation, storage, and further conversions resulting from conjugation with the substituent.

EXPERIMENTAL

IR spectra were recorded on a JASCO FT/IR 5300 spectrometer, and UV/vis spectra on a Shimadzu UV-2200 spectrometer. ^1H- and ^{13}C-NMR spectra were obtained with a Varian VXR-500 spectrometer at 500 MHz and 125 MHz, respectively, in a mixed solvent as designated. Chemical shifts are reported in parts per million (ppm) relative to $(CH_3)_4Si$ as an internal standard and coupling constants in Hz. FAB mass spectra were obtained on a JMS-AX505H mass spectrometer using *m*-nitrobenzylalcohol as a matrix. Halobenzene was dried over 4Å molecular sieves, and toluene over Na. 2-Silyloxy-1,3-dienes were purchased or prepared by the reported method for **1c-e**.[21] Diene precursors, hydroxy ester **5**, hydroxy ketone **8** and hydroxy nitrile **11** were prepared by the Baylis-Hilman reaction,[14] except for **14** and **17** which were prepared from 3-sulfolene.[18,19] The diester **20** was prepared by the reported method.[20] Flash chromatography for separation of products was performed on a silica gel column (Fuji-Davison 300 mesh) eluted with the solvent noted.

Diels-Alder Reaction of C_{60} with 2-Silyloxy-1,3-butadienes 1a-e: General Procedure.

A solution of C_{60} (20 mg, 0.028 mmol) and 2-silyloxy-1,3-diene **1** (0.042 mmol) in dry toluene (10 ml) was heated in a thick wall glass cylinder stoppered with a screw cap under a nitrogen atmosphere (temperature and time are indicated in Table 1). After evaporation of the solvent, the residue was dissolved in THF (6 ml) including 1 *N* HCl (0.4 ml) and the solution was stirred for 30 min. Removal of THF left a brown residue, which was dissolved in toluene, washed with aq. $NaHCO_3$, and dried over $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on a silica gel column eluted with hexane to remove unreacted C_{60} and then with toluene to give a 1:1 cycloadduct **2**. The yields are listed in Table 1. The spectral data for new compounds were observed as follows.

2c: FAB-MS m/z 866 (M^+), 720 (base peak); IR (KBr) ν (cm^{-1}) 2919, 1725, 1262, 1094, 1020, 700, 527; UV/vis (hexane) λ (nm) 432, 313, 269, 262, 255, 243, 217 ; ^1H-NMR ($CDCl_3/CS_2$, 1/1) δ 3.53 (dd, *J*=19.4 and 2.8 Hz, 1 H), 4.14 (d, *J*=15.0 Hz, 1 H), 4.20 (dd, *J*=19.4 and 14.0 Hz, 1 H), 5.07 (d, *J*=15.0 Hz, 1 H), 5.43 (dd, *J*=14.0 and 2.8 Hz, 1 H), 7.25-7.48 (m, 5 H); ^{13}C-NMR ($CDCl_3/CS_2$, 1/1) δ 45.12, 50.50, 52.73, 63.44, 69.01, 128.45, 134.43, 134.95, 135.57, 136.50, 137.57, 138.56, 139.07, 140.60, 140.74, 141.61, 141.62, 141.68, 141.94, 142.06, 142.08, 142.11, 142.33, 142.37, 142.84, 142.86, 142.88, 142.97, 143.31, 144.59, 144.66, 144.77, 144.80, 144.81, 144.93, 145.64, 145.72, 145.76, 145.79, 145.95, 145.98, 146.42, 146.44, 146.51, 146.56, 146.57, 146.69, 146.72, 146.75, 146.85, 146.91, 147.87, 147.92, 151.10, 153.69, 155.65, 156.22, 207.96.

2d: FAB-MS m/z 818 (M^+), 720 (base peak); IR (KBr) ν (cm^{-1}) 2927, 1721, 1426, 1225, 527; UV/vis (hexane) λ (nm) 432, 326, 313, 256, 212; ^{1}H-NMR (CDCl$_3$) δ 1.98 (br s, 3 H), 2.28 (br s, 3 H), 3.20 (br s, 1 H), 3.76 (br s, 1 H), 4.26 (br s, 1 H), 4.84 (br s, 1 H); ^{13}C-NMR spectrum (CDCl$_3$) δ 29.96, 31.20, 41.41, 52.87, 52.95, 63.17, 70.95, 134.53, 134.55, 139.15, 139.16, 139.18, 140.75, 141.63, 141.97, 142.00, 142.11, 142.47, 142.63, 143.01, 143.03, 143.54, 144.93, 145.02, 145.67, 145.72, 145.73, 145.78, 145.81, 146.17, 146.60, 146.64, 146.68, 146.85, 146.87, 146.92, 146.99, 147.02, 147.05, 147.06, 147.08, 147.10, 147.11, 147.12, 148.04, 148.13, 207.75.

2e: FAB-MS m/z 816 (M$^+$), 720 (base peak); IR (KBr) ν (cm^{-1}) 2922, 1730, 1426, 1262, 1026, 527; UV/vis (hexane) λ (nm) 432, 312, 255, 211; ^{1}H-NMR (CDCl$_3$/CS$_2$, 1/1) δ 2.60 (m, 1 H), 2.76 (m, 1 H), 3.26 (dd, *J*=19.5 and 3.0 Hz, 1 H), 3.30 (m, 1 H), 3.39 (m, 1 H), 3.68 (quintet, *J*=3.0 Hz, 1 H), 3.81 (t, *J*=3.0 Hz, 1 H), 3.95 (dt, *J*=19.5 and 3.0 Hz, 1 H); ^{13}C-NMR (CDCl$_3$/CS$_2$, 1/1) δ 23.61, 25.06, 42.47, 44.79, 55.43, 66.12, 67.12, 135.83, 136.26, 136.56, 137.04, 140.49, 140.60, 140.67, 141.81, 141.90, 141.93, 141.97, 142.08, 142.10, 142.14, 142.19, 142.22, 142.28, 142.30, 142.81, 142.82, 142.89, 143.22, 143.36, 143.41, 144.72, 144.78, 144.86, 144.92, 145.31, 145.34, 145.45, 145.66, 145.67, 145.69, 145.71, 145.78, 145.79, 145.90, 145.91, 146.44, 146.46, 146.49, 146.55, 146.61, 146.69, 146.74, 147.83, 147.84, 153.72, 154.28, 154.44, 211.60.

Reactivity of C$_{60}$ *vs.* C$_{70}$ toward Danishefsky's Diene 1b.

A solution of 1:1 mixture of C$_{60}$ and C$_{70}$ in dry toluene was heated at 60°C in the presence of 10 equiv. of **1b**, and consumed fullerenes were measured by HPLC (JASCO 880-PU, cosmosil packed column at 340 nm, toluene) at appropriate intervals. Relative amounts (%) of the remaining fullerenes *vs.* time (h) were plotted and the result is shown in Fig. 1.

Catalyzed Addition Reaction of 2a with Silyl Ketene Acetal 3.

To a solution of **2a** (34 mg, 0.043 mmol) and TiCl$_4$ (9 mg, 0.047 mmol) in dichloromethane (20 ml) was added silyl ketene acetal **3**[22] (10 mg, 0.048 mmol) in dichloromethane (10 ml) at -78°C. The mixture was stirred at this temperature for 4 h and quenched with aq. K$_2$CO$_3$. The product was extracted with toluene, and the combined extracts were washed with water, dried over MgSO$_4$, and evaporated to dryness. The residue was chromatographed on a silica gel column (hexane/toluene 1/2) to give recovered **2a** (10 mg) and **4** (8 mg, 20%): FAB-MS m/z 927 (M$^+$), 720 (base peak); IR (KBr) ν (cm^{-1}) 2924, 1736, 1460, 1262, 1098, 1024, 802, 527; UV/vis (hexane) λ (nm) 434, 308, 255, 215; ^{1}H-NMR (CDCl$_3$) δ 3.09 (ddd, *J*=15.0, 8.0 and 3.0 Hz, 1 H), 3.16 (ddd, *J*=15.0, 10.0 and 3.0 Hz, 1 H), 3.45 (ddd, *J*=14.0, 10.0 and 3.0 Hz, 1 H), 3.48 and 3.51 (d, *J*=17.0 Hz, each 1 H), 3.61 (ddd, *J*=14.0, 8.0 and 3.0 Hz, 1 H), 3.78 and 3.82 (d, *J*=14.5 Hz, each 1 H), 4.11 (s, 1 H), 7.20-7.47 (m, 5 H); ^{13}C-NMR (CDCl$_3$) δ 35.54, 37.49, 47.59, 49.21, 62.27, 64.47, 72.37, 121.74, 126.65, 129.90, 131.10, 135.27, 135.38, 135.63, 136.11, 140.48, 140.50, 140.56, 141.78, 141.81, 141.97, 142.02, 142.19, 142.23, 142.29, 142.30, 142.36, 142.37, 142.44, 142.80, 142.86, 142.89, 143.49, 143.55, 144.88, 144.98, 145.00, 145.07, 145.27, 145.54, 145.56, 145.68, 145.70, 145.72, 145.78, 145.80, 145.86, 146.07, 146.20, 146.48, 146.51, 146.55, 146.67, 146.69, 146.71, 146.75, 147.96, 147.98, 150.34, 156.35, 156.78, 156.99, 157.95, 171.44.

Diels-Alder Reaction of C$_{60}$ with Ethyl 2-Methylene-3-butenoate (6).

A solution of C$_{60}$ (477 mg, 0.66 mmol) and ester **5** (286 mg, 2 mmol) in *o*-dichlorobenzene (25 ml) was placed in a thick wall glass cylinder, and to this solution were added methanesulfonyl chloride (0.15 ml, 2 mmol) and triethylamine (0.55 ml, 4 mmol) successively under an argon atmosphere. After the cylinder was stoppered with a screw-cap, the mixture was stirred and heated at 150°C for 3 h. The resulted precipitates were filtered off and the solvent was further distilled under reduced pressure [80°C (bath temp.)/2 mmHg]. The brown residue was subjected to chromatography eluted with hexane/toluene(1/1) to give recovered C_{60} (150 mg) as the first fraction and the cycloadduct **7** (260 mg, 68% yield based on consumed C_{60}) as the second fraction[23]: FAB-MS m/z 846 (M^+), 720 (base peak); IR (KBr) ν (cm^{-1}) 2924, 1709, 1638, 1262, 1113, 748, 527; UV/vis (hexane) λ (nm) 432, 308, 255, 225, 213; ^1H-NMR ($CDCl_3$) δ 1.45 (t, J=7.5 Hz, 3 H), 4.20 (d, J=5.5 Hz, 2 H), 4.38 (s, 2 H), 4.44 (q, J=7.5 Hz, 2 H), 8.06 (t, J=5.5 Hz, 2 H); ^{13}C-NMR ($CDCl_3$) δ 14.64, 39.12, 41.34, 61.55, 65.43, 65.98, 128.47, 129.29, 135.85, 135.99, 136.28, 140.40, 140.48, 141.80, 141.91, 141.94, 142.32, 142.40, 142.47, 142.52, 142.87, 142.90, 143.42, 144.94, 145.03, 145.47, 145.69, 145.76, 145.79, 146.11, 146.53, 146.56, 146.81, 146.84, 147.96, 148.01, 156.73, 156.80, 165.60.

Diels-Alder Reaction of C_{60} with 3-Methylene-4-penten-2-one (9).

A solution of C_{60} (21 mg, 0.029 mmol) and ketone **8** (34 mg, 0.3 mmol)[24] in *o*-dichlorobenzene (3 ml) was placed in a thick wall glass cylinder, and to this solution were added methanesulfonyl chloride (34 mg, 0.3 mmol) and triethylamine (61 mg, 0.6 mmol) each dissolved in *o*-dichlorobenzene (0.5 ml) successively under an argon atmosphere. After the cylinder was stoppered with a screw-cap, the mixture was stirred and heated at 150°C for 30 min. The same work-up as above left a brown residue, which was subjected to chromatography eluted with toluene to give recovered C_{60} (5 mg) as the first fraction and the cycloadduct **10** (9 mg, 50% yield based on consumed C_{60}) as the second fraction: FAB-MS m/z 816 (M^+), 720 (base peak); IR (KBr) ν (cm^{-1}) 2922, 1672, 1630, 1427, 1260, 766, 527; UV/vis (hexane) λ (nm) 432, 322, 309, 255, 214; ^1H-NMR ($CDCl_3/CS_2$, 1/3) δ 2.67 (s, 3 H), 4.24 (d, J=5.5 Hz, 2 H), 4.32 (br s, 2 H), 7.91 (t, J=5.5 Hz, 2 H); ^{13}C-NMR ($CDCl_3/CS_2$, 1/3) δ 24.88, 36.93, 41.28, 65.09, 65.46, 135.31, 135.75, 140.16, 140.32, 140.85, 141.62, 141.71, 141.98, 142.15, 142.19, 142.59, 142.64, 143.06, 143.13, 144.56, 144.71, 144.77, 145.05, 145.33, 145.45, 145.46, 145.57(2C), 145.74, 146.24, 146.28, 146.49. 146.57, 147.60, 147.71, 156.07, 156.37, 194.43.

Diels-Alder Reaction of C_{60} with 2-Methylene-3-butenenitrile (12).

A solution of C_{60} (95 mg, 0.13 mmol) and nitrile **11** (32 mg, 0.33 mmol) in *o*-dichlorobenzene (5.5 ml) was placed in a thick wall glass cylinder, and to this solution were added methanesulfonyl chloride (38 mg, 0.33 mmol) and triethylamine (67 mg, 0.66 mmol) each dissolved in *o*-dichlorobenzene (0.5 ml) successively under an argon atmosphere. After heating and work-up as employed for **5**, the brown residue was subjected to chromatography eluted with hexane/toluene(3/7) to give recovered C_{60} (24 mg) as the first fraction and the cycloadduct **13** (39 mg, 49% yield based on consumed C_{60}) as the second fraction: FAB-MS m/z 799 (M^+), 720 (base peak); IR (KBr) ν (cm^{-1}) 2922, 2220, 1624, 1262, 1096, 802, 527; UV/vis (hexane) λ (nm) 431, 255, 214; ^1H-NMR ($CDCl_3/CS_2$, 1/3) δ 4.21 (d, J=6 Hz, 2 H), 4.24 (s, 2 H), 7.79 (t, J=6 Hz, 2 H); ^{13}C-NMR ($CDCl_3/CS_2$, 1/3) δ 40.90, 41.61, 64.68, 64.89, 117.17, 117.32, 135.60, 135.79, 140.30, 140.36, 141.70, 141.77, 142.05, 142.07, 142.11, 142.14, 142.69, 142.71, 143.18, 144.62, 144.68, 144.73, 144.79, 145.52, 145.54, 145.65, 145.72, 145.77, 146.31, 146.34, 146.61, 146.62, 147.34, 147.70, 147.74, 154.73, 155.22.

Diels-Alder Reaction of C_{60} with 2-(Phenylsulfonyl)-1,3-butadiene (15).

A solution of C_{60} (20 mg, 0.028 mmol) and sulfolene **14** (36 mg, 0.14 mmol) in chlorobenzene (6 ml) was placed in a thick wall glass cylinder. After the cylinder was stoppered with a screw-cap, the solution was stirred and heated at 135°C for 30 min under an argon atmosphere. Evaporation of the solvent left a brown residue, which was subjected to chromatography eluted with toluene to give recovered C_{60} (8 mg) as the first fraction and the cycloadduct **16** (12 mg, 79% yield based on consumed C_{60}) as the second fraction: FAB-MS m/z 914 (M^+), 720 (base peak); IR (KBr) ν (cm^{-1}) 2922, 1638, 1319, 1153, 615, 527; UV/vis (hexane) λ (nm) 432, 310, 256, 211; ^{1}H-NMR ($CDCl_3/CS_2$, 1/1) δ 4.22 (d, *J*=6 Hz, 2 H), 4.28 (s, 2 H), 7.47 (t, *J*=6 Hz, 1 H), 7.44-7.52 (m, 2 H), 8.04-8.09 (m, 3 H); ^{13}C-NMR ($CDCl_3/CS_2$, 1/1) δ 39.39, 40.76, 64.64, 65.15, 128.98, 129.40, 134.03, 135.31, 135.35, 138.75, 140.04, 140.05, 140.27, 141.63, 141.71, 141.99, 142.08, 142.67, 143.15, 144.61, 144.62, 144.65, 144.84, 145.38, 145.48, 145.50, 145.55, 145.59, 146.27, 146.30, 146.50, 146.56, 147.70, 154.59, 155.44.

Diels-Alder Reaction of C_{60} with 2-Nitro-1,3-butadiene (18).

A solution of C_{60} (30 mg, 0.042 mmol) and sulfolene **17** (24 mg, 0.15 mmol) in *o*-dichlorobenzene (3 ml) was placed in a thick wall glass cylinder. After the cylinder was stoppered with a screw-cap, the solution was stirred and heated at 140°C for 10 min under an argon atmosphere. Evaporation of the solvent left a brown residue, which was subjected to chromatography eluted with hexane/toluene (3/1) to give recovered C_{60} (1 mg) as the first fraction and the cycloadduct **19** (12 mg, 36% yield based on consumed C_{60}) as the second fraction: FAB-MS m/z 819 (M^+), 720 (base peak); IR (KBr) ν (cm^{-1}) 2922, 1655, 1522, 1335, 723, 527; UV/vis (hexane) λ (nm) 431, 311, 255, 215; ^{1}H-NMR ($CDCl_3/CS_2$, 1/3) δ 4.31 (d, *J*=6 Hz, 2 H), 4.69 (s, 2 H), 8.19 (t, *J*=6 Hz, 1 H); ^{13}C-NMR ($CDCl_3/CS_2$, 1/3) δ 38.35, 41.18, 64.73, 65.59, 134.59, 135.60, 135.64, 140.29, 140.37, 141.71, 141.78, 142.04, 142.06, 142.11, 142.17, 142.69, 142.72, 143.17, 144.58, 144.68, 144.70, 144.76, 145.52, 145.54, 145.69, 145.75, 146.30, 146.33, 146.60, 146.63, 147.69, 147.74, 151.69, 154.73, 155.06.

Diels-Alder Reaction of C_{60} with Dimethyl 2,6-Cyclohexadiene-1,2-dicarboxylate (20).

A solution of C_{60} (30 mg, 0.042 mmol) and diene **20** (122 mg, 0.62 mmol) in *o*-dichlorobenzene (3 ml) was placed in a thick wall glass cylinder. After the cylinder was stoppered with a screw-cap, the solution was stirred and heated at 180°C for 8 h under an argon atmosphere. Evaporation of the solvent left a brown residue, which was subjected to chromatography eluted with toluene to give recovered C_{60} (21 mg) as the first fraction and the cycloadduct **21** (3 mg, 27% yield based on consumed C_{60}) as the second fraction: FAB-MS m/z 916 (M^+), 720 (base peak); IR (KBr) ν (cm^{-1}) 2924, 1723, 1640, 1267, 527; UV/vis (hexane) λ (nm) 432, 310, 255, 216; ^{1}H-NMR ($CDCl_3/CS_2$, 5/1) δ 2.37 (m, 2 H), 3.28 (m, 2 H), 3.97 (s, 6 H), 4.59 (s, 2 H); ^{13}C-NMR ($CDCl_3/CS_2$, 5/1) δ 25.25, 45.81, 52.73, 69.19, 136.26, 136.97, 140.02, 140.21, 141.55, 141.75, 141.77, 141.82, 142.00, 142.10, 142.45, 142.58, 142.60, 143.05, 143.15, 144.61, 144.63, 145.24, 145.38, 145.40, 145.42, 145.54, 145.70, 145.75, 145.79, 146.24, 146.44, 146.54, 147.61, 154.24, 154.67, 165.93, 198.96.

Calculations.

FMOs of typical dienes and dienophiles and C_{60} (Table 2) were calculated using MNDO PM3 by HyperChem® 4.0 (HyperCube Inc.) on IBM-PC compatible computer.

ACKNOWLEDGMENT

This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (No. 05233105) from the Ministry of Education, Science and Culture.

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23. A post-eluent was obtained by continuous elution, and it became a major product when 5 equiv. of reagent was employed. The structure was assumed to be a 1:2 cycloadduct on the basis of FAB-MS peaks at m/z 972 (M^+), 846 (M^+ - CH_2=CH-C(COOEt)=CH_2) and 720 (base peak), and IR absorption bands at 1713 and 527 cm^{-1}; however, the detailed structure was not determined.
24. Ketone **8** was prepared by employing aqueous conditions as described in ref. 15, but it was difficult to obtain it in a pure form. Therefore, the reaction was conducted using a large excess of crude reagent which was first purified as far as possible by chromatography.

(*Received* 23 *June* 1995)