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Convenient Syntheses of 6,5 Open and 6,6 Closed Cycloalkylidenefullerenes

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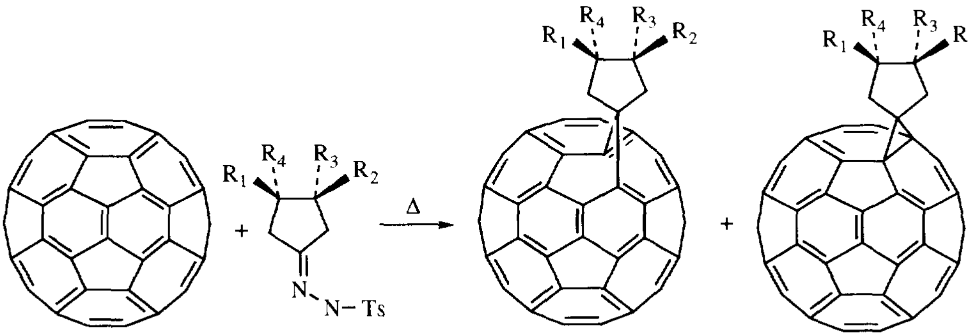
Abstract: A number of cycloalkylidenefullerenes have been prepared by reaction of C_{60} with tosylhydrazone lithium salts in refluxing toluene. Short reaction times lead to high yields of 6,5 open methanofullerenes which subsequently rearrange to the 6,6 closed isomers. Copyright © 1996 Elsevier Science Ltd

The addition of carbenes and carbene transfer reagents to C_{60} provides a convenient route to the methanofullerenes.[1] Of the four possible methanofullerenes, only the 6,5 open and the 6,6 closed isomers have been reported with the 6,6 the more thermodynamically stable and the 6,5 often formed faster.[2] We have taken advantage of the reported methanofullerene formation by tosylhydrazone salts[3] to generate a series of cycloalkylidenefullerenes. These reactions permit the simple synthesis of functionalized cycloalkylidene fullerenes with well defined geometries. In many cases, we find that reaction conditions can be chosen such that high yields of the 6,5 open cycloalkylidenefullerene result after short reaction times.

For example, C_{60} and the tosylhydrazone lithium salt **1a**[4] were refluxed in toluene for 12 h resulting in a 71% conversion of C_{60} to a mixture of mixture of carbene adducts of which 20% were the mono adducts **2a** and **3a** formed in a 2:1 ratio. However, shortening the reaction time to 1.5 h results in a 75% conversion of C_{60} to adducts of which 53% is the mono adduct **2a**. There is no evidence for **3a** in the nmr spectrum of the crude



1a; $R_1=R_2=CO_2Et$, $R_3=R_4=H$
b; $R_1=R_3=CO_2Et$, $R_2=R_4=H$
c; $R_1=R_3=CO_2Me$, $R_2=R_4=H$
d; $R_1=R_2=R_3=R_4=H$

2
(6,5 Open)

3
(6,6 Closed)

reaction mixture or in the spectrum of chromatographically purified **2a**. The use of 12-crown-4 to increase the solubility of the tosylhydrazone lithium salt decreases the reaction time but also results in the formation of more 6,6 mono adduct, **3a**. Table 1 gives reaction conditions, yields and 6,5:6,6 cycloalkylidenefullerene ratios for the reaction of a number of tosylhydrazone lithium salts with C_{60}.

Table 1. Products of the reaction C_{60} with lithium salts of tosylhydrazones in refluxing toluene.

Lithium Salt	Ratio of C_{60} to Lithium Salt	Time (min)	12-crown-4 added	Conversion of C_{60} (%)	% Yield of Monoadducts	**2**:**3** ratio (by NMR)
1a	1:1.2	720	No	71	20	2:1
1a	1:2	90	No	75	53	*
1a	1:3	25	Yes	71	36	5.6:1
1a	3:1	17	Yes	14	50	2.1:1
1b	1:2	90	No	78	60	9:1
1b	1:2	15	No	25	50	24:1
1c	1:1	90	No	38	23	1.7:1
1c	1:3	25	Yes	50	67	13.3:1
1d	1:2	90	No	60	40	4:1
1d	1:4	25	Yes	20	15	2.8:1
1d	1:4	8	Yes	15	10	6.7:1
4	1:4	8	Yes	15	11	2.8:1
5	1:2	90	No	80	70	13.3:1

*The 6,6 closed isomer could not be detected by nmr.

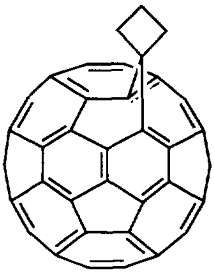
It seems reasonable to propose that the initial carbene transfer reaction generates the 6,5 open adducts which rearrange to the 6,6 closed compounds under the reaction conditions. Rearrangements of other 6,5 to 6,6 methanofullerenes have been observed[1,2c,3c] and the kinetics of one such rearrangement have been reported.[2c] We find that heating **2a** in refluxing toluene results in a clean conversion to **3a**. Since the conversion of pure **2a** to **3a**, which takes 60 h to go to completion, is considerably slower than that observed under the conditions of the formation of **2a**, it appears that a component of the reaction mixture catalyses the conversion.[5]

Spectral data confirm the structure of these adducts. Characteristically, the 6,5 adducts show the protons above the former 5 membered ring absorbing ~2.5 ppm downfield of the protons above the former 6 membered ring while the protons in the 6,6 adducts absorb in between those of the 6,5 adduct. Table 2 lists the chemical shifts of the alpha protons in the cycloalkylidene annulenes and cyclopropanes prepared in this investigation. in all cases, the number of different alpha protons is that expected from the symmetry of the adduct and the substitution on the cycloalkylidene moiety. The 6,6 adducts are further distinguished by the signals for the bridgehead carbons at ~80 ppm. In **3a** these nonequivalent carbons resonate at 80.9 and 82.9 ppm while in **3b** they are equivalent and absorb at 81.4 ppm. In all cases the 6,5 adducts show a uv spectrum identical to that of C_{60} while the 6,6 adducts have a characteristic absorbtion at 432 nm. Adducts **2** and **3** all show molecular ion or m+1 peaks in their FAB mass spectrum.

Table 2. Chemical Shifts (ppm) of α Protons in Cycloalkylidenefullerenes

Cycloalkylidene Annulene			Cycloalkylidene Cyclopropane	
Adduct	α Protons above former five membered ring	α Protons above former six membered ring	Adduct	α Protons above 6 membered rings
2a	4.36(dd,J=6.97Hz, J=13.52Hz,1H) 3.87(dd,J=8.00Hz, J=13.56Hz,1H) (in C_6D_6)	2.17(dd,J=7.22Hz, J=13.84Hz,1H) 1.66(dd,J=8.30Hz, J=13.82Hz,1H) (in C_6D_6)	**3a**	3.37(m, 2H) 3.15(m, 2H) (in $CDCl_3$)
2b	4.43(dd,J=8.40Hz J=13.41Hz,1H) (in $CDCl_3$)	2.14(dd,J=8.65Hz J=13.76Hz,1H) 1.93 (dd,J=9.14Hz J=13.72Hz,1H) (in $CDCl_3$)	**3b**	3.30(m,2H) 3.17(m,2H) (in $CDCl_3$)
2c	4.59(dd,J=8.50Hz, J=13.46Hz, 1H) 4.08(dd,J=9.41Hz, J=13.34Hz,1H) (in $CDCl_3$)	2.17(dd,J=8.61Hz, J=13.72Hz,1H) 1.91(dd,J=9.53Hz, J=13.77Hz, 1H) (in $CDCl_3$)	**3c**	3.25(m, 2H) 3.10(m, 2H) (in $CDCl_3$)
2d	3.93(t,J=7.16Hz,2H) (in CS_2)	2.10(t,J=7.58Hz,2H) (in CS_2)	**3d**	3.28(m, 4H) (in CS_2)
6	3.99(t,J=7.7Hz,2H) (in CS_2)	2.18(t,J=8.01Hz,2H) (in CS_2)	**8**	3.19(t, J=7.71Hz 4H) (in CS_2)
7	3.73(broad,2H) (in CS_2)	2.12(broad,2H) (in CS_2)	**9**	2.66(broad,2H) (in CS_2)

Reaction of the lithium salts of cyclobutanone and cyclohexanone tosylhydrazones, **4** and **5**, with C_{60} generates the corresponding 6,5 open (**6** and **7**) and 6,6 closed (**8** and **9**) cycloalkylidenefullenes (Table 2). Although cyclobutylidenefullerenes **6** and **8** were not separated from one another and from unreacted C_{60}, heating the reaction mixture resulted in complete conversion to **8**. Both cyclobutylidenes show m+1 peaks at 775 in the FAB mass spectrum. The alpha protons above the former 5 and 6 membered rings in the cyclobutylidene annulene **6** are separated by 1.8 ppm. The alpha protons in both of the cyclohexylidenefullerenes **7** and **9** are broad multiplets presumably due to flipping of the cyclohexane ring. Protons over the former 5 and 6 membered rings in **7** are separated by 2 ppm.



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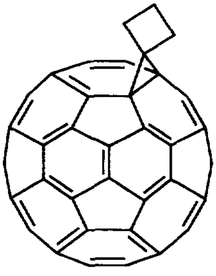

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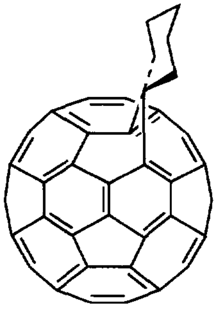

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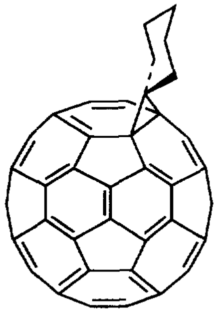

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Reactions of this type should facilitate the synthesis of fullerene derivatives with well defined geometries and specifically positioned functional groups.

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