Pergamon

Tetrahedron Letters, Vol. 37, No. 12, pp. 2049-2052, 1996

0040-4039/96 $15.00 + 0.00

S0040-4039(96)00215-8

Introduction of Two Benzyl Groups to C_{60} by Using the Collman Reagent

Sadao Miki,* Masunori Kitao, and Koushi Fukunishi

Department of Chemistry and Materials Technology, Kyoto Institute of Technology,
Matsugasaki, Sakyo-ku, Kyoto 606, Japan

Abstract: Addition of C_{60} to a suspension of the Collman reagent in THF gave a strongly colored but almost transparent solution. Treatment of the resulting solution with benzyl bromide gave a C_{60} derivative possessing two benzyl groups. The ^{1}H-NMR as well as the ^{13}C-NMR of the product indicated that the reaction site was 1, 4-position.

Fullerene and its derivatives have been a subject of much recent interest from the viewpoints of basic organic chemistry as well as their potentiality in a wide range of materials sciences. In this context, the development of methods for introducing carbon atomic groups to C_{60} is an important target. Addition of Grignard or organolithium reagents to C_{60} [1] is an efficient method [2] for alkyl derivatization of C_{60}. However, the products obtained by this method were limited to relatively unstable alkylhydrofullerenes $RC_{60}H$ obtained by the protonation of the alkylated C_{60} anion (RC_{60}^-); an exception was the interesting reaction of R_3SiCH_2MgCl with C_{60} to give bis-alkylated compounds.[3] Although it seems possible to obtain bis-alkylated C_{60} by the reaction of RC_{60}^- with carbon electrophiles, the only reaction of this type known so far is that where tropylium ion was used as an electrophile.[4] We report here our study on the introduction of two benzyl groups to C_{60} by using the Collman reagent.

In a typical run, a suspension of the Collman reagent (46.0 mg)[5] in dry THF (15 mL) was added to a suspension of C_{60} (155 mg) in the same solvent (5 mL) at room temperature, and the mixture was stirred for 10 min to afford a strongly colored, reddish-brown solution. Upon adding benzyl bromide (0.051 mL), the color of the solution turned brown gradually, and a brown precipitate appeared. The entire procedure was carried out under argon atmosphere in an appropriately designed glassware. After stirring for 18 h, the supernatant liquid of the reaction mixture was collected by centrifugal separation. The remaining solid materials were washed several times with benzene by sonification, and the supernants obtained were collected. The combined supernant was subjected to HPLC so that the product formation as well as the recovery of C_{60} were analyzed quantitatively. The HPLC showed the formation of one predominant major product (**1**) (13% = 32% based on C_{60} consumed) and recovery of C_{60} (60%). Solvent removal followed by chromatography on silica gel with cyclohexane gave a powdery product (**1**), which was purified by reprecipitation from a chloroform solution with pentane.

The UV/Vis spectrum of the product (**1**) in cyclohexane is shown in Fig. 1. The intense bands at λ_{max} = 213, 256 and 327 are very similar to those of C_{60}. This behavior has been observed throughout the mono adducts of C_{60}.[6] A characteristic feature of the UV/Vis spectrum of **1** is that a new broad band with a relatively

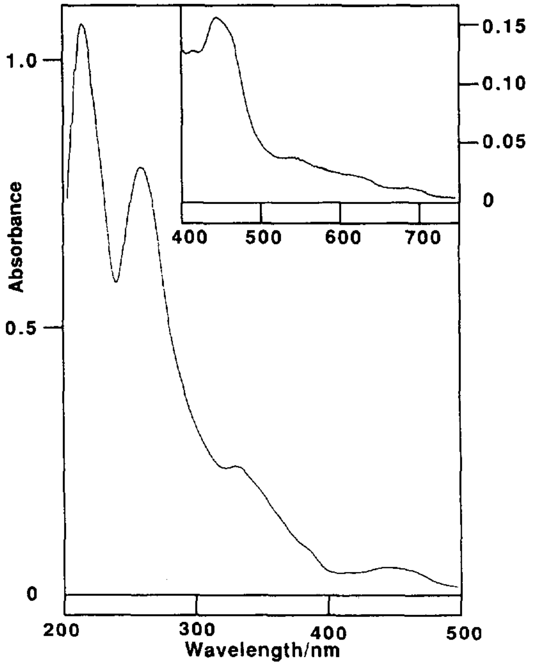


Figure 1 UV/Vis spectrum of the reaction product (**1**) in cyclohexane, [**1**] = 1.11 x 10^{-5} mol/L.

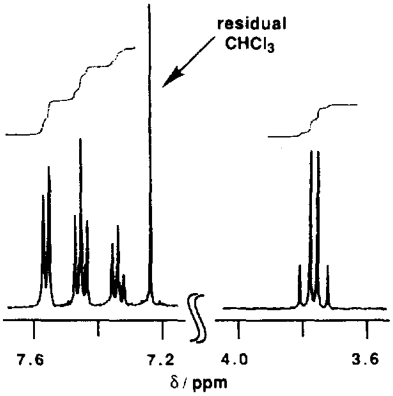
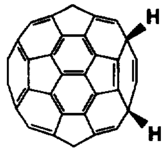
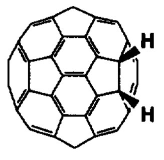


Figure 2 ^{1}H-NMR (400 MHz) spectrum of the reaction product (**1**) in $CDCl_3$.

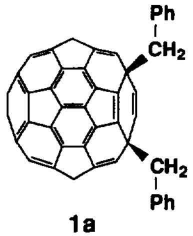
large extinction coefficient ($\varepsilon = 5400$) appears at $\lambda_{max} = 443$ nm. In the ^{1}H-NMR (400 MHz) spectrum of the product (Fig. 2), an AB quartet with a typical geminal coupling constant (J_{HH} = 17.4 Hz) appeared at 3.77 ppm (center of the quartet) in addition to a set of signals for *p*-, *m*-, and *o*-protons of phenyl group at 7.57, 7.45, and 7.34 ppm, respectively. The ^{1}H-NMR spectrum as well as a mass spectrum (M = 902) suggest that the product is a C_{60} derivative possessing two benzyl groups. The benzyl protons appeared as an AB quartet. This fact indicates that the two benzyl groups are introduced to magnetically equivalent carbons, and the two carbons are asymmetric to cause the magnetic diastereotopicity of the NMR of the benzyl protons. This means that the molecule possesses a plane of symmetry which perpendicularly bisects an axis formed with the two quaternary aliphatic carbons in the C_{60}. In the ^{13}C-NMR (Fig. 3), the signals for the carbons of the C_{60} skeleton appeared in the region of 137.9 - 157.9 ppm (31 signals) and at 60.6 ppm (one signal). In addition to these resonances, signals for the benzyl groups were observed at 29.7, 127.6, 128.5, 131.1, 136.3 ppm. The number of the ^{13}C-NMR signals of 32 for the carbons of the C_{60} skeleton suggests the C_S or C_2 symmetry of the molecule. A semiempirical calculation indicates that among the possible isomers of dihydro-C_{60} possessing C_S or C_2 symmetry, 1,4-$C_{60}H_2$ and 1,6-$C_{60}H_2$ are the structures of significantly low energy.[7a] Several theoretical studies predict that the 1,4-adduct is energetically more preferable than the 1,6-adduct.[7] Thus, on the basis of energetical feasibility the 1,4 -adduct (**1a**) is considered as the most plausible structure for the reaction product.[8] Actually, the diagnostically low field ^{13}C-NMR at 157.9 ppm for the reaction product shows a strong resemblance to that (157.7 ppm) for the well defined 1,4-adduct, $C_{60}[CH_2Si(O^iPr)Me_2]_2$.[3]



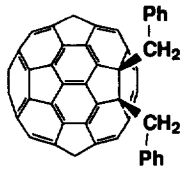
1,4-$C_{60}H_2$



1,6-$C_{60}H_2$

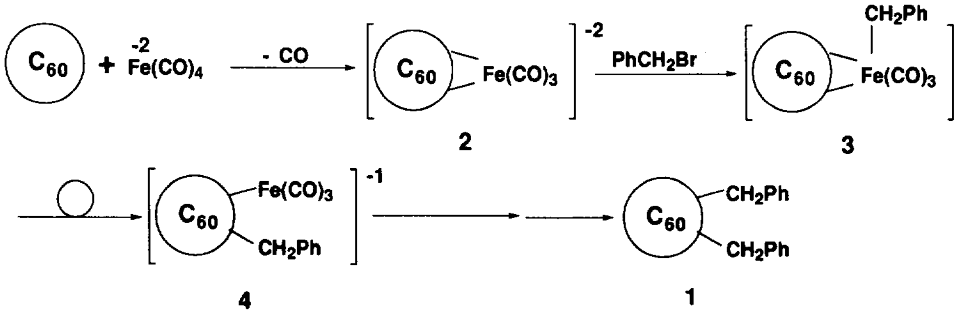


1a



1b

Though we lack definite proof at present, we consider Scheme 1 as a plausible reaction mechanism, that is, as follows : the reaction of C_{60} with the Collman reagent gives an iron-C_{60} adduct (**2**) due to the strong nucleophilicity of the reagent, the so-called supernucleophile.[9,10] The oxidative addition of benzyl bromide to the iron atom of **2** followed by the migration of the benzyl group to C_{60} gives **4**. Repetition of a series of the reactions starting from **4** would give the final product. It is well known that in the reaction of the Collman reagent with alkyl halides, an alkyl group on the iron atom migrates to one of the carbonyl ligands to form an acyl-iron bond.[11] In the present case of **2**, it seems likely that the low-lying vacant orbitals of the C_{60} skeleton might facilitate the migration of the benzyl group to the C_{60}. Similar migration of an anionic ligand on the iron atom to the coordinated ethylene has been reported.[12] Another mechanism can be considered, that is, the formation of the C_{60} dianion by an electron transfer from the Collman reagent to C_{60} followed by alkylation of the dianion. Though alkylation of the electrochemically generated dianion of C_{60} with iodomethane was known,[13] methylated products were not obtained when iodomethane was employed in place of benzyl bromide in the present reaction.



Scheme 1

Bis-alkylation of C_{60} by using simple alkyl halides such as bromoethane and iodomethane was attempted. However, in these cases only the recovery of C_{60} was observed. The reason might be as follows. The reactivity of the iron atom in **2** toward oxidative addition is reduced significantly compared with the iron atom of the Collman reagent, because two negative charges in **2** are delocalized over the C_{60} moiety as is the case of the alkyl fullerenide anion. Therefore, the steps of oxidative addition do not proceed easily for simple alkyl halides. In the case that 1,2-bis(bromomethyl)benzene was used in place of benzyl bromide, the same product as the adduct of C_{60} with *ortho*-quinodimethane reported by Mullen[2b] was obtained as a major product in 20% yield with recovery of a large amount of C_{60}. It seems that the 1,4-elimination reaction to give *ortho*-quinodimethane proceeds much faster than the migration of the benzyl group to C_{60} in the intermediate of the type of **3**. Although the versatility of the method remains to be elucidated, the present reaction is a rare example of the introduction of two carbon groups to C_{60}. Further studies are in progress.

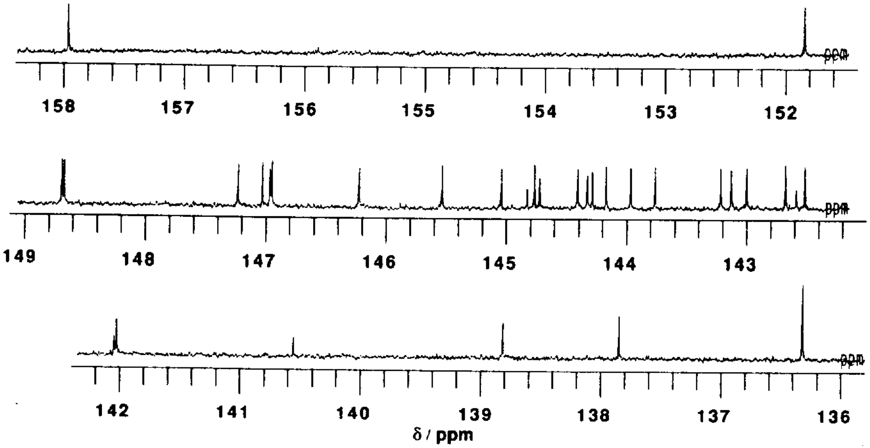


Figure. 3 ^{13}C-NMR ($CDCl_3$) signals for the carbons of the C_{60} skeleton in the reaction product (**1**). The signal (60.6 ppm) for the aliphatic quaternary carbon is not shown. The signal at 136.3 ppm is derived from the phenyl groups.

Acknowledgment

This work was supported by a Grant-in-Aid on Priority-Area-Research " Photoreaction Dynamics" (06239106) and a Grant-in Aid for Scientific Research (04203221) from the Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES AND NOTES

1. Hirsch, A.; Soi, A.; Karfunkel, R. *Angew. Chem. Int. Ed. Engl.* **1992**, 31, 766-768. Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, 114, 9697-9699. Komatsu, K.; Murata, Y.; Takimoto, N.; Mori, S.; Sugita, N.; Wan, T. S. M. *J, Org. Chem.* **1994**, 59, 6101-6102.
2. Reactions of C_{60} with carbenes or ortho-quinodimethane are also attractive methods for the derivatization of the skeleton. (a) Wudl, F. *Acc. Chem. Res.* **1992**, 25, 157-161and references cited therein. Eiermann, M.; Wudl, F.; Prato, M.; Maggini, M. *J. Am. Chem. Soc.* **1994**, 116, 8354-8365; (b) Belik, P.; Gugel, A.; Spickmann, J.; Mullen, K. *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 78-80.
3. Nagashima, H.; Terasaki, H.; Kimura, E.; Nakajima, K.; Itoh, K. *J. Org. Chem.* **1994**, 59, 1246-1248.
4. Kitagawa, T.; Tanaka, T.; Tanaka, Y.; Takeuchi, K.; Komatsu, K. *J. Org. Chem.* **1995**, 60, 1490-1491.
5. Collman reagent was prepared according to the method reported in reference 9.
6. Hirsch, A.; Grosser, T.; Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, 126, 1061-1067
7. (a) Mitsuzawa, N.; Dixon, D. A.; Fukunaga, T. *J. Phys. Chem.* **1992**, 96, 7594-7604. (b) Henderson. C. C.; Rohlfing, C. M.; Cahill, P. A. *Chem Phys. Lett.* **1993**, 213, 383-388. (c) Yoshida, Z.; Dogane, I.; Ikehira, H.; Endo, T. *Chem Phys. Lett.* **1993**, 201, 481-484.
8. We appreciate discussions with Professor F. Wudl (UCSB) who suggested 1,4-adduct for our reaction product at the 3rd International Symposium on Functional Dyes (1995).
9. Colmann, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, 99, 2515-2526.
10. A neutral complex of C_{60} with iron carbonyl has been reported ; Douthwaite, R. E.; Green, M. L. H.; Stephens, A. H. H.; Turner, F. C. *J. Chem. Soc. Chem. Comm.*, **1993**, 1522-1523.
11. Collman, J. P. *Acc. Chem. Res.* **1975**, 8, 342-347.
12. Cooke, Jr. M. P.; Parlman, R. M. *J. Am. Chem. Soc.* **1975**, 97, 6863-6865.
13. Carton, C.; Subramanian, R.; D'Souza, F.; Kim, J.; Kutner, W.; Jones M. T.; Kadish, K. M*J. Am. Chem. Soc.* **1993**, 115, 8505-8506.

(*Received in Japan* 20 *December* 1995; *revised* 29 *January* 1996; *accepted* 1 *February* 1996)