Pergamon

Tetrahedron Letters, Vol. 37, No. 7, pp. 1085-1086, 1996

0040-4039/96 $15.00 + 0.00

0040-4039(95)02256-2

Synthesis and Characterisation of the Methanofullerenes, $C_{60}(CHCN)$ and $C_{60}(CBr_2)$

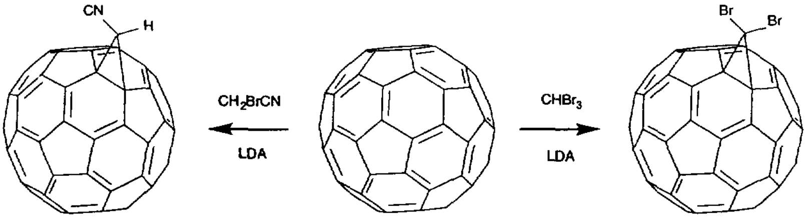
Ana M. Benito, Adam D. Darwish, Harold W. Kroto, Mohammed F. Meidine,
Roger Taylor and David R. M. Walton

School of Chemistry and Molecular Sciences,
University of Sussex
Brighton BN1 9QJ, U.K.

Abstract: Two new methanofullerenes, $C_{60}(CHCN)$ and $C_{60}(CBr_2)$, have been prepared by treating a mixture of [60]fullerene and either CH_2BrCN or $CHBr_3$ respectively with LDA. The products were purified by silica gel column chromatography, characterised by EI-MS and IR, and shown by ^{13}C NMR to consist solely of 6-6 ring junction adducts.

The chemistry of [60]fullerene has undergone sustained and rapid development since 1990.[1-2] The first methanofullerene, $C_{60}(CPh_2)$, was described by Wudl *et al.*[3] in the following year and this area of synthetic endeavour has proved to be particularly fruitful ever since.[4] It offers a practicable route to diverse organofunctional fullerenes,[5] as well as providing a promising solution to one of the most difficult problems associated with fullerene chemistry, namely controling the extent of multiple additions to the cage.[6] In a few instances,[7] methano-bridging (accompanied by valence isomerization) occurs at the [6,5]-ring junctions in [60]fullerene, resulting in an open transannular bond (giving a homofullerene), however in most cases, including the two new compounds reported here, the [6,6] addition mode (cyclopropane ring formation) predominates.

In this letter we describe the preparation of two new methanofullerenes, $C_{60}(CHCN)$ and $C_{60}(CBr_2)$, obtained by adding LDA to a toluene solution of [60]fullerene and a 10-fold excess of CH_2BrCN or $CHBr_3$ respectively. Initial experiments using NaH as base[5] were unsuccessful, and we therefore chose LDA as an alternative, because it has been recommended for α-metallation of nitriles[8] and because, in our hands, it does not appear (unlike n-BuLi)[2] to react with [60]fullerene. (*e.g.* Treatment of [60]fullerene with a 10-fold excess of LDA in toluene solution at -78 °C followed by aqueous work-up led to quantitative recovery of [60]fullerene).



1', 1'-Dibromo-1,2-methano[60]fullerene $C_{60}(CBr_2)$.- A 100 cm^3 round bottom flask, fitted with a subaseal cap and side arm, was charged with [60]fullerene (100 mg, 0.14 mmol) and repeatedly purged with dry nitrogen. Anhydrous toluene (60 cm^3) followed by $CHBr_3$ (351.4 mg, 14 mmol) was added and the mixture was stirred magnetically until the [60]fullerene dissolved to give a magenta solution. The flask was then cooled to - 78 °C in a dry ice/acetone bath and a freshly prepared solution of LDA (14 mmol) in hexane/THF was added by means of a syringe. The solution became brown immediately. The bath was removed and stirring was continued for 3 h. A few drops of HCl (0.1 M) were then added and, following 1 h additional stirring, the toluene layer was extracted with water, dried ($MgSO_4$) and concentrated by evaporation under reduced pressure. An EI-MS of the crude product revealed the presence of mono (M^+ 892), together with trace quantities of bis adducts (M^+ 1064). Column chromatography on silica-gel using 2/1 n-hexane/toluene as eluent, followed by removal of the solvent *in vacuo* gave the pure monoadduct $C_{60}CBr_2$ (40%) as a brown solid (m.p. > 350 °C). The ^{13}C n.m.r. spectrum[9] [CS_2-$CDCl_3$; 0.02M $Cr(acac)_3$] exhibited singlets at δ 79.79 (2C), corresponding to the cyclopropane ring cage carbons, and at δ 32.32 (1C) for the bridgehead carbon (CBr_2), together with 16 resonances (13 x 4C; 3 x 2C) in the δ 145.45 - 139.25 region, comensurate with the C_{2v} symmetry associated with the [6,6] adduct.

1'-Cyano-1,2-methano[60]fullerene $C_{60}(CHCN)$.- An identical 14 mmol scale experiment, using CH_2BrCN in place of $CHBr_3$ resulted in a mixture (EI-MS analysis) of the mono adduct, together with traces of bis, and tris adducts: peaks at 759, 798 and 837 (M^+) respectively. The monoadduct, $C_{60}CHCN$ (15%) was separated in the same way (column chromatography, silica gel, 1/1 n-hexane/toluene as eluent) and isolated as a brown solid (m.p. > 350 °C). The FTIR spectrum (KBr pellet) displays a weak band at 2243 cm^{-1}, ν ($C\equiv N$) together with bands at: 1632 and 1463 cm^{-1}, ν (CH); 1427, 1183, 572 and 526 cm^{-1} (fullerene vibrations). ^1H n.m.r. spectrum [CS_2-$CDCl_3$] δ 4.62 (s), $J_{C\text{-}H}$ = 177.8 Hz.. ^{13}C n.m.r. spectrum[10] [CS_2-$CDCl_3$]: δ 113.16 ($\underline{C}N$); δ 63.36 (2C), cyclopropane ring cage carbons; δ 22.9 (1C), bridgehead carbon ($\underline{C}HCN$); 30 resonances [1 x 4C (not fully resolved); 25 x 2C; 4 x 1C] in the δ 146.00 - 137.40 region commensurate with C_s symmetry.

The successful introduction of nitrile and of bromines as cyclopropane ring substituents usefully extends the range of methanofullerenes containing bridgehead functional groups (*eg.* COOR[5], Aryl[11], $C\equiv CTMS$[12], Cl[13]) , and we are currently exploring the synthetic potential of these new systems.

Acknowledgments. We thank the C.S.I.C. for the award of the Postdoctoral Fellowship (to AMB) and the EPSRC for financial support.

References

1. Taylor, R.; Walton, D.R.M. *Nature* **1993**, 363, 685-693.
2. Hirsch, A. *The Chemistry of the Fullerenes*; Georg Thieme Verlag: Stuttgart, **1994**.
3. Suzuki, T; Li, Q.; Khemani, K.C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, 254, 1186-1188.
4. Diederich, F.; Isacs, I;. Philp, D. *Chemical Society Reviews* **1994**, 23, 243-255.
5. Bingel, C. *Chem.Ber.* **1993**, 126, 1957-1959.
6. Hirsch, A.; Lamparth, I.; Karfunkel, H.R. *Angew.Chem. Int. Ed. Engl.* **1994**, 33, 437-438.
7. Suzuki, T.; Li Q.; Khemani, K.C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, 114, 7301-7302.
8. Ahlbrecht, H.; Pfaff, K. *Synthesis* **1978**, 897.
9. ^{13}C n.m.r. (125.76 MHz) signals in the fullerene region. δ 145.45 (2), 145.37 (2), 145.36 (2), 144.89 (1), 144.87 (2), 144.75 (2), 144.64 (2), 144.36 (1), 143.78 (2), 143.44 (2), 143.24 (2), 142.88 (1), 142.33 (2), 142.18 (2), 141.24 (2), 139.25 (2).
10. ^{13}C n.m.r. (125.76 MHz) signals in the fullerene region. δ 146 (2), 145.59 (2), 145.51 (2), 145.47 (2), 145.44 (2), 145.17 (2), 145.09 (2), 145.08 (2), 145.07 (2), 145.05 (2), 144.92 (2), 144.81 (2), 144.56 (2), 144.55 (1), 144.42 (1), 143.98 (2), 143.89 (2), 143.30 (2), 143.17 (4), 143.10 (2), 143.09 (1), 143.05 (1), 142.53 (2), 142.26 (2), 142.22 (2), 142.15 (2), 141.43 (2), 141.40 (2), 139.06 (2), 137.40 (2). The signal at 143.17 ppm could not be resolved.
11. Suzuki, T.; Li, Q.; Khemani, K.C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, 114, 7300-7301.
12. Anderson, H.L.; Faust, R.; Rubin, Y.; Diederich, F. *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1366-1368 .
13. Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *Tetrahedron Letters* **1993**, 34, 6911-6912.

(*Received in UK* 9 *November* 1995; *revised* 22 *November* 1995; *accepted* 24 *November* 1995)