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MECHANOCHEMICAL ARYLATION AND ALKYLATION OF FULLERENE C_{60} UNDER THE SOLVENT-FREE CONDITIONS

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Abstract: The mechanochemical reaction of fullerene C_{60} with organic bromides and alkali metals was found to give the corresponding aryl or alkyl C_{60} derivatives under the solvent-free conditions.

Organic reactions under solvent-free conditions have been actively investigated in recent years.[1] However, not much attention has been paid to a rather classical mechanochemical technique such as ball milling, which has been applied mainly to inorganic or metallic materials.[2] Previously, a mechanochemical technique which we call "the high-speed vibration milling (HSVM)" has been successfully employed for functionalization of fullerene C_{60} such as addition of the α-bromoester in the presence of zinc,[3] [4+2] cycloaddition of condensed aromatics,[4] and [2+2] dimerization of C_{60} itself.[5] In this communication we report the applicability of the

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HSVM method to the reaction of C_{60} with aryl and alkyl bromides in the presence of alkali metals under the solvent-free reaction conditions.

As a general procedure, C_{60} (20 mg), aryl or alkyl bromide (**1a-e**), and sodium metal in a molar ratio of 1 : 2~3 : 4~6 were placed in a stainless-steel capsule together with a stainless-steel milling ball under an atmosphere of nitrogen. These materials were vigorously mixed for 30 min by shaking the capsule at the speed of 3500 rpm by the use of a high-speed vibration mill.[5b] The resulting black powdery reaction mixture was quenched with trifluoroacetic acid in *o*-dichlorobenzene. The analysis of the product mixture by high-pressure liquid chromatography (HPLC) indicated the formation of one main product and a small amount (< 3%) of fullerene dimer C_{120}.[6] Separation by flash chromatography or by preparative HPLC afforded some amount of unreacted C_{60} and arylated or alkylated C_{60} derivatives **2a-e** (Scheme). The structures of **2b**,[7] **2c**,[8] and **2e**[9] were confirmed by comparison of the MS and ^{1}H NMR data with reported data while those of **2a** and **2d** were determined based on the MS, UV-vis, ^{1}H NMR, and ^{13}C NMR data.

The results of the reactions are summarized in Table. The formation of either the C_{60} polymer[5b] or the C_{60} dimer (C_{120})[5b] is suppressed by the presence of the bromide. As shown by entry 1 and 9-11 for bromide **1a** and by entry 3 and 6-8 for bromide **1c**, potassium and lithium metals were found to be effective as sodium while magnesium was not so effective.

In the control experiments we confirmed that the starting materials were recovered unchanged by the HSVM treatment of mixtures of C_{60} and bromides **1a-e**. On the other hand, when bromide **1d** was similarly treated with sodium metal, the Wurtz-type reaction[10] took place to give 1,1'-biadamantyl in 29.9% yield in addition to adamantane in 11.5% yield.

Scheme

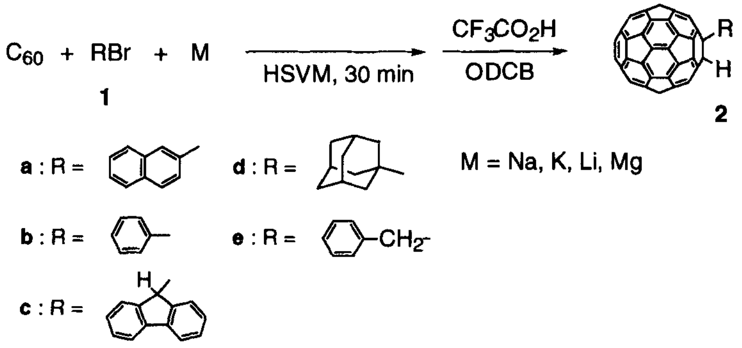

Table. Reaction of C_{60} and Organic Bromides with Metals by the HSVM Technique

entry	RBr[a]	Metal[b]	HPLC analysis[c] C_{60} : $RC_{60}H$ (%)	C_{60} recov.(%)[d]	$RC_{60}H$ (**2**) yield (%)[d]
1	**1a**	Na	25 : 27	12.8	20.5
2	**1b**	Na	47 : 24	32.1	9.4
3	**1c**	Na	34 : 37	30.7	24.2
4	**1d**	Na	58 : 10	43.3	5.8
5	**1e**	Na	58 : 12	49.0	5.6
6	**1c**	K	55 : 20	44.9	19.1
7	**1c**	Li	45 : 15	24.4	11.4
8	**1c**	Mg	71 : 3	–[e]	–[e]
9	**1a**	K	63 : 21	–[e]	–[e]
10	**1a**	Li	18 : 21	–[e]	–[e]
11	**1a**	Mg	93 : 2	–[e]	–[e]

[a] 2-3 equiv relative to C_{60}. [b] 4-6 equiv relative to C_{60}. [c] Peak area ratio determined by HPLC analysis using Cosmosil Buckyprep column with toluene as an eluent detected at 326 nm. [d] Isolated yield. [e] Separation was not performed.

Thus in conclusion the present work demonstrated the feasibility of functionalization of C_{60} by a simple mechanochemical treatment with organic bromides and alkali metals under solvent-free conditions although the product yield was not high.

Experimental

General. NMR spectra were recorded on a Varian Mercury-300 spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C). UV-vis spectra were recorded with a Shimadzu UV-2100PC spectrometer. APCI mass spectra were measured on a Finigan-MAT TSQ 700 spectrometer. HPLC analysis was conducted on a Shimadzu LC-10AD chromatograph, detected at 326 nm, equipped with a Cosmosil Buckyprep column (4.6 mm × 250 mm) using toluene as an eluent. Preparative HPLC was performed using a Cosmosil 5PBB column (10 mm × 250 mm) with *o*-dichlorobenzene as an eluent.

High-speed vibration milling. Throughout the present study, we used a mill which consisted of a capsule and a milling ball made of stainless-steel (Fe-Cr-Ni with a composition of 74:18:8 by weight). The capsule containing the milling ball was fixed in a home-built vibrating machine so that the capsule was shaken along its long axis horizontally with a slight fluctuation (rotating motion) at a rate of 3500 cycles per min.

Typical procedure for the preparation of 1-(2-Naphthyl)-1,2-dihydrofullerene (2a). In a glove box filled with nitrogen, C_{60} (20.3 mg, 0.0282 mmol), 2-bromonaphthalene (11.8 mg, 0.0570 mmol), and sodium (3.5 mg, 0.152 mmol) were weighed into a stainless-steel capsule containing a milling ball. The capsule was vigorously shaken for 30 min by the use of a high-speed vibration mill. The black powdery reaction mixture was washed into 10 mL of *o*-dichlorobenzene containing 0.05 mL of trifluoroacetic acid (0.65 mmol) and the mixture was filtered through a filter-paper. The filtrate was evaporated under reduced pressure to give a dark brown solid. The mixture was dissolved in 4 mL of CS_2 and separated by flash chromatography over silica gel eluted with hexane-CS_2 (2:1) to give C_{60} (2.6 mg, 12.8%) and compound **2a**.(4.9 mg, 20.5%): ^1H NMR (CS_2-$CDCl_3$ (2:1)) δ 8.77 (d, 1H), 8.69 (dd, J = 8.7 Hz, 1H), 8.31 (d, J = 8.7 Hz, 1H), 8.09 (m, 1H), 8.04 (m, 1H), 7.65 (m, 2H), 6.85 (s, 1H); ^{13}C NMR (CS_2-$CDCl_3$ (2:1)) δ 153.41, 152.31, 147.31, 147.08, 146.66, 146.24, 146.20, 146.04, 146.01, 145.81, 145.63, 145.46, 145.37, 145.24, 145.20, 145.05, 144.48, 144.37, 143.11, 142.12, 141.88, 141.85, 141.77, 141.50, 141.44, 140.21, 140.09, 136.20, 135.82, 133.66, 132.63, 130.22, 128.22, 127.77, 127.00, 126.65, 125.82, 125.40, 67.96, 63.58; UV-vis (cyclohexane) λ_{max} (nm) (log ε) 211 (5.15), 226 (5.13), 256 (5.03), 308 (4.53), 325 (4.51), 434 (3.56), 703 (2.53); MS (-APCI) *m/z* 848 (M).

1-(1-Adamantyl)-1,2-dihydrofullerene (2d). ^1H NMR (CS_2-$CDCl_3$ (2:1)) δ 6.77 (s, 1H), 2.83 (m, 6H), 2.52 (m, 3H), 2.08 (m, 6H); ^{13}C NMR (CS_2-$CDCl_3$ (2:1)) δ 154.36, 153.25, 147.62, 147.14, 146.96, 146,89, 146.11, 145.97, 145.88, 145.60, 145.13, 145.08, 144.44, 144.28, 143.01, 142.42, 142.39, 141.98, 141.82, 141.44, 141.38, 141.22, 140.19, 138.64, 136.36, 136.21, 74.05, 55.41, 42.97, 39.47, 37.23, 29.54; UV-vis (cyclohexane) λ_{max} (nm) (log ε) 211 (5.03), 257 (4.91), 326 (4.41), 433 (3.55), 705 (2.58); MS (-APCI) *m/z* 856 (M).

References and Notes

1. Metzger, J. O. *Angew. Chem. Int. Ed.* **1998**, *37*, 2975.
2. For few examples of applications to organic reactions, see: Braun, T.; Buvaribarcza, A.; Barcza, L.; Konkolythege, I.; Fodor, M.; Migali, B. *Solid State Ionics,* **1994**, *74*, 47. Rowlands, S. A.; Hall, A. K.; McCormick, P. G.;

Street, R.; Hart, R. J.; Ebell, G. F.; Donecker, P. *Nature* **1994**, *367*, 223. Im, J.; Kim, J.; Kim, S.; Hahn, B.; Toda, F. *Tetrahedron Lett.* **1997**, *38*, 451. Field, L. D.; Sternhell, S.; Wilton, H. V. *Tetrahedron* **1997**, 53, 4051.

3. Wang, G-W.; Murata, Y.; Komatsu, K.; Wan, T. S. M. *Chem. Commun.* **1996**, 2059.
4. Murata, Y.; Kato. N.; Fujiwara, K.; Komatsu, K. *J. Org. Chem.*, in press.
5. (a) Wang, G-W.; Komatsu, K.; Murata, Y.; Shiro, M. *Nature* **1997**, *387*, 583. (b) Komatsu, K.; Wang, G-W.; Murata, Y.; Tanaka, T.; Fujiwara, K.; Yamamoto, K; Saunders, M. *J. Org. Chem.* **1998**, *63*, 9358.
6. The HSVM treatment of C_{60} with a small amount (< 0.5 molar equivalent) of sodium is known to give a mixture of C_{120} and C_{60} (about 30%:70%): ref 5b.
7. Hirsch, A.; Grösser, T.; Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, *126*, 1061.
8. Murata, Y.; Komatsu, K.; Wan, T. S. M. *Tetrahedron Lett.* **1996**, *37*, 7061.
9. Chen, J.; Cai, R-F.; Huang, Z-E.; Wu, H-M.; Jiang, S-K.; Shao, Q-F. *J. Chem. Soc., Chem. Commun.* **1995**, 1553.
10. Reinhardt, H. F. *J. Org. Chem.* **1962**, *27*, 3258.

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