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Novel solvent-free reaction of C_{60} with active methylene compounds in the presence of Na_2CO_3 under high-speed vibration milling

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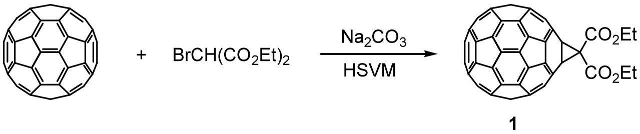
Abstract—Inorganic base, Na_2CO_3, was utilized to replace organic base, DBU, in the Bingel reaction employing diethyl bromomalonate under the mechanochemical 'high-speed vibration milling' conditions to give the cyclopropanated C_{60} **1** in high yield. In contrast, reactions of C_{60} with diethyl malonate and ethyl acetoacetate in the presence of Na_2CO_3 under HSVM conditions afforded 1,4-bisadduct **2** and dihydrofuran-fused C_{60} derivative **3**, respectively. © 2003 Elsevier Science Ltd. All rights reserved.

Solvent-free organic reactions have drawn great interest, particularly from the viewpoint of green chemistry, because harmful organic solvents are not involved in the production process.[1] Moreover, some novel products can be obtained only from solvent-free reactions rather than from the liquid-phase reactions, especially in the field of fullerene chemistry. A mechanochemical technique called high-speed vibration milling (HSVM) was first applied to the solvent-free Reformatsky-type reaction of C_{60} in 1996.[2] Since then this HSVM technique has been successfully utilized in the first synthesis of fullerene dimer C_{120},[3a,b] cross-dimer C_{130},[3c] and trimer C_{180},[3d,e] [4+2] reaction of C_{60} with condensed aromatics,[4] with phthalazine[5] and with di(2-pyridyl)-1,2,4,5-tetrazine,[6] reaction of C_{60} with dichlorodiphenylsilane and lithium,[7] and reaction of C_{60} with organic bromides and alkali metals.[8] In this paper, we report the novel solvent-free reactions of C_{60} with active methylene compounds in the presence of Na_2CO_3 under HSVM conditions.

The reaction of C_{60} with halogenated active methylene compounds such as α-halo esters or α-halo ketones in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (the Bingel reaction) is one of the most widely applied reactions in fullerene chemistry to give various cyclopropanated derivatives of fullerenes.[9] When we tried to extend the HSVM technique to the solvent-free reaction of C_{60} with diethyl bromomalonate and DBU, no desired product was formed. However, the expected product was obtained when the organic base (DBU) was replaced by inorganic base (Na_2CO_3). When a mixture of C_{60} (28.8 mg), ethyl bromomalonate and Na_2CO_3 in 1:1:1 molar ratio was vigorously milled for 30 min, monoadduct **1** was obtained in 51% (86% based on consumed C_{60}) yield along with 7% (12% based on consumed C_{60}) of bisadducts (Scheme 1).

$NaHCO_3$ can also be used as the base, but the yield was slightly lower. This is the first example of the use of inorganic weak base in the Bingel reaction, which was conducted under the solvent-free conditions. The reaction is considered to follow the well-established mechanism of the Bingel reaction involving the first



Scheme 1.

Keywords: C_{60}; active methylene compounds; Na_2CO_3; solvent-free; high-speed vibration milling.

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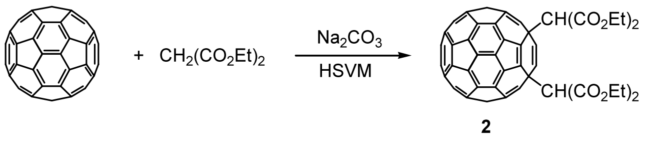


Scheme 2.

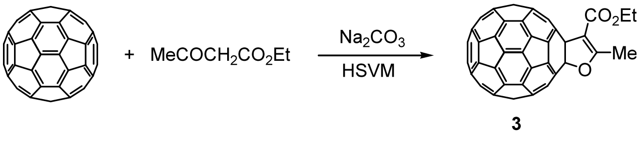
nucleophilic attack of the carbanion. The advantage of this solid-state reaction lies in the feasibility of conducting the reaction in a much larger scale. Actually we have conducted this solid-state Bingel reaction under the HSVM conditions using 0.5 g of C_{60} and obtained the monoadduct **1** in 40–50% and bisadduct in 15–20% with C_{60} recovered in about 20%.

In order to see what would happen if the leaving group such as the bromo group is absent, diethyl bromomalonate was replaced by diethyl malonate in the above reaction under HSVM conditions. To our surprise, a totally different product was obtained. Thus, the reaction of C_{60} (43.2 mg[10]), diethyl malonate and Na_2CO_3 in 1:1:1 molar ratio afforded the novel 1,4-bisadduct **2** in 18% (82% based on consumed C_{60}) after a 1 h treatment under the HSVM conditions (Scheme 2). Previously a reaction of lithium fluorenide with C_{60} in THF was shown to give the 1,4-bisadduct when oxygen was introduced to cause one-electron oxidation of the initially formed functionalized C_{60} anion to its radical.[11] The present result is considered to involve the radical addition pathway in a similar manner.[12]

The structure of adduct **2** was identified by its MS, ^1H, ^{13}C NMR, FT-IR, and UV–vis spectra.[13] The atmospheric pressure chemical ionization (APCI) mass spectroscopy operated in negative-ion mode exhibited the molecular ion peak at m/z 1038. Reflecting that the two $CH(CO_2Et)_2$ groups are attached to the chiral carbon, both the ^1H and ^{13}C NMR spectrum of **2** displayed two sets of signals for the $CO_2CH_2CH_3$ group. In addition to these signals, the ^{13}C NMR showed 30 signals including two overlapping ones for the C_{60} skeleton, consistent with the C_s symmetry of the 1,4-adduct structure. The UV–vis spectrum exhibited a broad absorption at 446 nm, which is diagnostic for a 1,4-adduct.[11]

The 1,4-bisadduct **2** was regioselectively formed probably because the bulky $CH(CO_2Et)_2$ group prohibited the formation of 1,2-bisadduct. Theoretical calculations by B3LYP/6-31G/HF/3-21G revealed that 1,4-bisadduct **2** is the most stable one among the four isomers of 1,2-, 1,4-, 1,6-, and 1,16-bisaddition patterns: the 1,4-bisadduct is more stable than the 1,2-, 1,16-, and 1,6-bisadducts by 3.3, 11.2, 22.3 kcal mol^{-1}, respectively.

In contrast, the reaction of C_{60} (43.2 mg[10]) with ethyl acetoacetate and Na_2CO_3 in 1:1.5:1.5 molar ratio for 30 min under HSVM conditions was found to give the dihydrofuran-fused C_{60} derivative **3** in 22% (49% based on converted C_{60}) (Scheme 3). No trace of the cyclopropanated derivative or 1,4-adduct was obtained.[14]



Scheme 3.

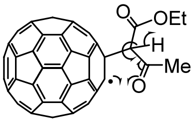


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Figure 1. Structure of radical **4** showing the followed intramolecular cyclization process.

Compound **3** was fully characterized by MS, ^1H, ^{13}C NMR, FT-IR, and UV–vis spectra.[15] The ^{13}C NMR and FT-IR of compound **3** match nicely with those of the dihydrofuran-fused C_{60} derivative obtained from the liquid-phase reaction of C_{60} with *tert*-butyl acetoacetate and piperidine in chlorobenzene,[16] supporting the assigned structure of **3**.

Again, it is supposed that the anion first formed is oxidized by oxygen[14,17] to the corresponding radical **4** (Fig. 1), which undergoes intramolecular cyclization and release of a hydrogen radical to give the dihydrofuran derivative **3**.

In conclusion, inorganic weak base, Na_2CO_3, was used to replace organic base, DBU, in the solvent-free Bingel reaction for the first time. Reaction of C_{60} with active methylene compounds having no halogen atom in the presence of Na_2CO_3 under HSVM conditions afforded products, which are totally different from the normal Bingel adduct, i.e. 1,4-bisadduct and dihydrofuran-fused C_{60} derivative, possibly through an one-electron transfer pathway.

Acknowledgements

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10. In each run, 14.4 mg of C_{60} was used, and the combined reaction mixture from three runs was separated on silica gel to afford the product along with unconverted C_{60}.
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12. Control experiments showed that no reaction occurred when air was completely excluded.
13. Spectral data of **2**: ^{1}H NMR (300 MHz, CS_2-$CDCl_3$) δ 5.01 (s, 2H), 4.48–4.38 (m, 4H), 4.31 (q, $J=7$ Hz, 4H), 1.38 (t, $J=7$ Hz, 6H), 1.28 (t, $J=7$ Hz, 6H); ^{13}C NMR (75 MHz, CS_2-$CDCl_3$) δ 166.06 (COO, 2C), 165.56 (COO, 2C), 152.00 (2C), 148.24 (2C), 148.02 (2C), 147.54 (2C), 147.06 (2C), 146.54 (2C), 146.41 (2C), 146.28 (2C), 145.03 (2C), 144.65 (2C), 144.58 (2C), 144.23 (2C), 144.13 (2C), 143.77 (2C), 143.74 (3C), 143.56 (2C), 143.20 (2C), 142.75 (2C), 142.68 (2C), 142.66 (4C), 142.42 (2C), 142.09 (1C), 141.92 (2C), 141.66 (1C), 141.41 (2C), 140.37 (2C), 140.14 (1C), 139.09 (2C), 138.67 (2C), 61.89 (OCH_2CH_3, 2C), 61.70 (OCH_2CH_3, 2C), 60.82 (*C*H, 2C), 55.47 (*sp*^{3}-*C*, 2C), 13.64 (OCH_2CH_3, 2C), 13.59 (OCH_2CH_3, 2C). UV–vis λ_{max} (THF) 256, 328, 446 nm; MS (-APCI) *m*/*z* 1038; FT-IR (KBr) ν 2980 (m), 2933 (w), 1755 (s), 1734 (s), 1460 (m), 1442 (m), 1430 (m), 1390 (m), 1368 (s), 1308 (s), 1263 (m), 1232 (s), 1210 (s), 1184 (s), 1153 (s), 1112 (m), 1096 (m), 1030 (s), 913 (m), 874 (w), 860 (w), 774 (w), 762 (w), 732 (m), 701 (w), 654 (w), 582 (w), 570 (m), 528 (s) cm^{-1}.
14. Another unknown compound was isolated in 4.2 mg. Control experiments showed that the yield of **3** decreased to 9% (4.6 mg) and the unknown product was isolated in 5.0 mg along with 73% of recovered C_{60} when the HSVM reaction was conducted under a nitrogen atmosphere.
15. Spectral data of **3**: ^{1}H NMR (400 MHz, CS_2-$CDCl_3$) δ 4.31 (q, $J=7$ Hz, 2H), 2.86 (s, 3H), 1.30 (t, $J=7$ Hz, 3H); ^{13}C NMR (100 MHz, CS_2-$CDCl_3$) δ 168.52 (COO, 1C), 163.43 (OCCH_3), 147.99 (2C), 147.48 (1C), 146.81 (2C), 146.76 (1C), 145.90 (2C), 145.68 (2C), 145.61 (2C), 145.47 (2C), 145.41 (2C), 145.11 (2C), 144.85 (2C), 144.63 (2C), 144.48 (2C), 144.22 (2C), 143.99 (2C), 143.88 (2C), 143.69 (2C), 142.28 (2C), 142.25 (2C), 142.16 (2C), 142.03 (2C), 141.92 (2C), 141.80 (2C), 141.76 (2C), 141.05 (2C), 140.93 (2C), 139.37 (2C), 138.87 (2C), 136.94 (2C), 134.77 (2C), 104.59 (*C*COO, 1C), 102.33 (*sp*^{3}-*C*O, 1C), 71.83 (*sp*^{3}-*C*C, 1C), 60.22 (OCH_2CH_3, 1C), 15.36 (OCCH_3, 1C), 14.28 (OCH_2CH_3, 1C); λ_{max} (THF) 254, 314, 426, 685 nm; MS (-APCI) *m*/*z* 848; FT-IR (KBr) ν 2978 (m), 2952 (w), 2900 (w), 1702 (s), 1642 (s), 1540 (w), 1462 (w), 1426 (m), 1392 (w), 1372 (s), 1325 (s), 1301 (m), 1273 (w), 1258 (w), 1174 (m), 1155 (w), 1127 (s), 1100 (s), 1016 (m), 975 (s), 947 (s), 930 (m), 883 (w), 848 (w), 834 (w), 795 (m), 779 (w), 765 (m), 731 (w), 696 (w), 606 (m), 574 (m), 528 (s), 476 (m).
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