Isomerically Pure Organo[60]fullerenes from $C_{60}{}^{2-}$ Salt: Synthesis and Characterization of 1-Benzyl-2-hydro[60]fullerene

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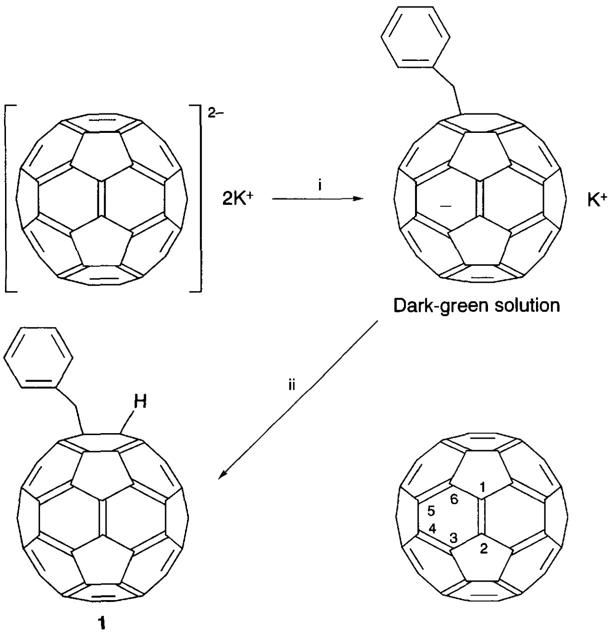
Isomerically pure 1-benzyl-2-hydro[60]fullerene is synthesized in 64% yield by the reaction of $C_{60}{}^{2-}$ potassium salt with benzyl chloride in THF at 50 °C.

There are many reactions for functionalizing C_{60}.[1] Of these, however, little attention has been paid to the chemistry of [60]fullerene anions and no isomerically pure organo[60]fullerenes have so far been obtained from $C_{60}{}^{n-}$ precursors.[2]

Recently, we developed a convenient preparation of $A_nC_{60}(THF)_m$ (A = K, Na) by reaction of alkali metal/1-methylnaphthalene with C_{60} in THF at room temp.[3,4] Some of these salts [such as $K_nC_{60}(THF)_m$, $n = 1–3$] are very soluble in THF ($4–6 \times 10^{-3}$ mol dm^{-3}) and the solutions can be stored under argon for at least one month. Since 1-methylnaphthalene is generally inert and easy to remove, the $C_{60}{}^{n-}$ solution produced *in situ* can be used directly for further reactions. These merits encouraged us to investigate the chemistry of $A_nC_{60}(THF)_m$ in detail. Here, we report the synthesis of 1-benzyl-2-hydro[60]fullerene **1** from $C_{60}{}^{2-}$ potassium salts, which, to our knowledge, represents the first synthesis of isomerically pure organo[60]fullerenes from $C_{60}{}^{n-}$ salts. We chose the benzyl adduct of C_{60} as the target compound because, despite many previous efforts,[5] no isomerically pure benzyl adduct of fullerenes has been isolated and fully characterized using other synthetic routes.

Compound **1** was prepared as follows (Scheme 1): under argon, a combination of C_{60} (240 mg, 0.33 mmol), potassium (26 mg, 0.67 mmol) and 1-methylnaphthalene (1 ml) was stirred in 50 ml THF for 3–4 h to produce a dark red–orange solution. 1 ml $ClCH_2Ph$ (in large excess) was added and the resulting mixture was stirred at 50 °C over 4 h. After centrifugation, 5 ml $MeCO_2H$ was added to the dark-green solution to give a brown precipitate. The product was washed with Et_2O and dried in vacuum to afford 217 mg of a dark brown powder. FAB-MS, ^1H NMR and ^{13}C NMR spectra ($CS_2/CDCl_3$, 300 and 150 MHz, respectively) indicate that the product contains trace C_{60} [no multiadducts such as $C_{60}(CH_2Ph)_2$ can be detected in this crude product] and can be easily purified by silica gel flash chromatography [toluene/hexane (*v*/*v*): C_{60}, 5 : 95, **1**, 45 : 55] to afford pure **1**† (174 mg, 64% yield). δ 6.67 for C_{60}-H in ^1H NMR of **1** (Fig. 1) suggests that the location of H atom is at C-2.[6] The assigned C_s structure for **1** is further supported by the ^{13}C NMR spectrum (Fig. 2), which consists of 28 lines of intensity 2 (including three pairs of coincident 2C peaks) and two lines of intensity 1 in the region between δ 154.81 and 135.36 (δ 136.03 is the signal of the benzyl group).

Theoretical studies[7] have pointed out that owing to Jahn–Teller effect,[8] the negative charges of $C_{60}{}^{2-}$ are localized mainly at 20 carbon atoms along an equatorial line of the molecule. Moreover, if the counterion effect is considered, the negative charges should be more localized, giving rising to considerable enhancement of both reactivity and selectivity of $C_{60}{}^{2-}$.



Scheme 1 *Reagents and conditions*: i, $ClCH_2Ph$, THF, 50 °C, over 4 h; ii, $MeCO_2H$

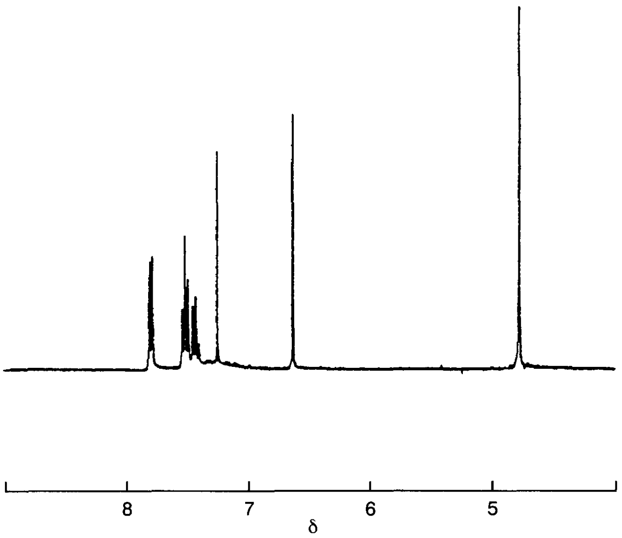


Fig. 1 ^1H NMR spectrum of **1** [300 MHz, $CS_2/CDCl_3$ (3 : 1)]

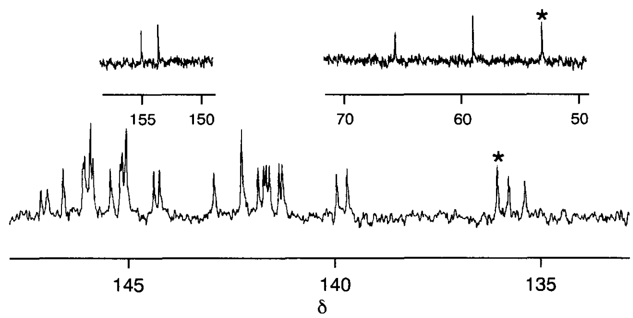


Fig. 2 The expanded ^{13}C NMR region of [60]fullerene C-atoms in **1** [150 MHz, $CS_2/CDCl_3$ (4 : 1)]. * Indicates benzyl carbons.†

While $C_{60}R^-$ salt is soluble in THF, both C_{60} and $C_{60}R_2$ are insoluble in this solvent. So any such impurities can be removed simply by centrifugation.

The tendency of $C_{60}R^-$ to react further with organic halides XR is dependent on the strength of the X–R bond, steric and electronic factors of R groups and the reaction conditions. For example, whereas electrochemical reaction of $C_{60}{}^{2-}$ with excess ICH_3 at room temp. gives mainly bisadduct $C_{60}Me_2$ (mixture of two isomers),[2b] the $C_{60}(CH_2Ph)^-$ in our case is stable (this species, however, can react smoothly with $ClSiMe_3$ at room temp. to afford novel dialkylated[60]fullerene with two different R groups, Jian Chen *et al.*, unpublished results) even when exposed to a large excess of benzyl chloride at a temperature as high as 50 °C. From these results we expect that full utilization of the diverse and unique chemical reactions of $C_{60}{}^{2-}$ and other [60]fullerene anions will open a new window for selective functionalization of C_{60}.

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Footnote

† *Spectroscopic data* for **1**: FAB-MS: 813 (M^+), 720 ($M^+ - CH_3C_6H_5$); ^1H NMR (300 MHz, $CS_2/CDCl_3$ (3 : 1)): δ 4.81 (s, 2H, CH_2), 6.67 (s, 1H, C_{60}-H), 7.48 (m, 1H, Ar-H), 7.56 (m, 2H, Ar-H), 7.84 (d, 2H, Ar-H); ^{13}C NMR [150 MHz, $CS_2/CDCl_3$ (4 : 1)]: δ 52.99 (CH_2), 58.87 (CH in C_{60} core), 65.50 (quaternary C in C_{60} core), 127.58 [CH(aryl)], 128.56 [CH(aryl)], 131.06 [CH(aryl)], 136.03 [C(aryl)], 135.36, 135.76, 139.68, 139.94, 141.28, 141.35, 141.58, 141.66, 141.72, 141.86, 142.92, 144.25, 144.39, 145.15, 145.20, 145.44, 145.85, 146.06, 146.08, 146.58, 153.36, 154.81 (C_{60}, 22 lines of 2C), 142.26, 145.06, 145.92 (C_{60}, three pairs of coincident 2C peaks), 146.97, 147.12 (C_{60}, two lines of 1C); UV–VIS (toluene, 400–900 nm): 706 nm (ε *ca.* 4.3 × 10^2 dm^3 mol^{-1} cm^{-1}), 433 (4.0 × 10^3), FTIR (KBr): 3017 cm^{-1}(w), 2998(w), 2965(w), 2912(w), 2845(w), 1493(w), 1458(w), 1427(m), 1258(w), 1214(w), 1183(m), 1155(w), 1117(w), 1067(w), 1029(w), 964(w), 807(m), 760(m), 744(m), 722(m), 697(s), 685(w), 663(w), 575(s), 563(m), 547(m), 525(vs), 512(m), 475(w).

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