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Efficient cyclopropanation of C_{60} starting from malonates

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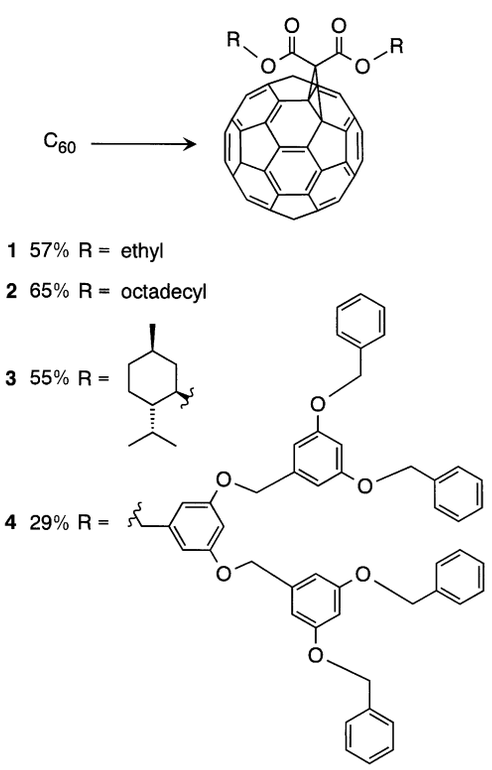
The direct treatment of C_{60} with malonates in the presence of CBr_4 and diazabicyclo[5.4.0]undec-7-ene (DBU) leads to an efficient conversion to methanofullerenes, which is demonstrated with the syntheses of monoadducts and highly symmetric hexaadducts in good yields.

Cyclopropanation of fullerenes *via* the reaction with bromomalonates in the presence of base is one of the most efficient tools for the synthesis of methanofullerenes.[1–8] The advantages of this reliable method of fullerene functionalisation are: (i) mild reaction conditions providing comparatively high yields, (ii) exclusive formation of [6,6]-bridged adducts and (iii) facile one step access to higher adducts (bis up to hexakis) with a stereochemically defined addition pattern using template activation with 9,10-dimethylanthracene (DMA).[4] Hence, unprecedented and aesthetically pleasing molecular architectures based on the C_{60} core are easily accessible with this reaction type.[4,5] Further side chain chemistry on such fullerene adducts opens up additional methods of fullerene functionalisation.[9]

Unfortunately, the preparation of bromomalonates is complex in some cases. First of all, the yields of bromomalonates are limited due to the simultaneous formation of dibromomalonates. Moreover, the chromatographic properties of starting malonates, bromo- and dibromo-malonates differ only slightly, especially when malonates with large side chains like dendrimers are used.[4c] This makes separation of the products impossible in many cases. Although, since the bromomalonate is the only reactive species, a mixture of malonate, bromo- and dibromo-malonate can be used as the reagent for cyclopropanation, however, the final purification of the desired fullerene adducts may be severely complicated. A modification of this cyclopropanation, namely the direct treatment of C_{60} with malonates in the presence of iodine and base[6] works satisfactorily only in some cases, *e.g.* with diethyl malonate. However, when we used other malonates containing dendritic or long alkyl side chains, the yields of monoadducts were very low and most of the C_{60} was converted into an unidentified material.

We now show that clean conversion of C_{60} into methanofullerenes in good yields can be achieved by direct treatment of the fullerene with malonates in the presence of CBr_4 and DBU. The synthesis of monoadducts is demonstrated with four different malonates, including chiral and sterically demanding dendritic side chains[4c] (Scheme 1) using the following general procedure. To a mixture of 100 mg of C_{60} (0.139 mmol), 69 mg (0.208 mmol) of CBr_4 and 0.208 mmol of the desired malonate, 32 μl (0.415 mmol) of DBU was added. After 6 h the different products were purified by flash chromatography. The identity of the newly synthesized compounds **2** and **3** was proven by their spectroscopic data.† The yields of monoadducts **1**–**4** are comparable or even better than those obtained by the corresponding reaction with the bromomalonates.[1,4c] For example, direct treatment of C_{60} with diethyl malonate gives 57% and the



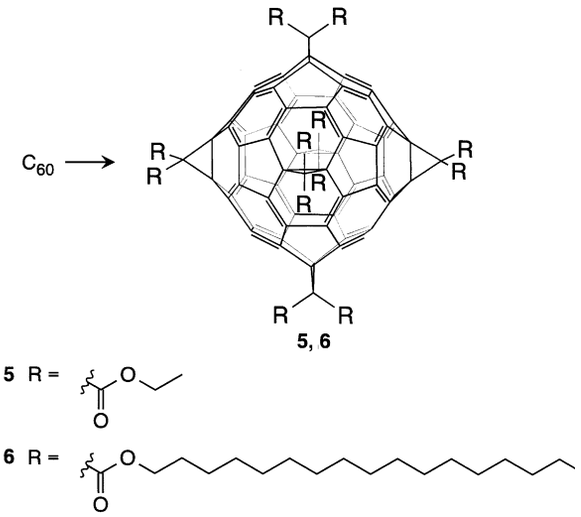
Scheme 1 *Reagents and conditions:* $CH_2(CO_2R)_2$ 1.5 equiv., CBr_4 1.5 equiv., DBU 3 equiv., toluene, room temp., 6 h

† Selected spectroscopic data of the newly synthesized compounds **2**, **3** and **6**.

2: $\lambda_{max}(CH_2Cl_2)$/nm 257.5, 325.5, 426.0; ν_{max}(KBr)/cm^{-1} 2953.5, 2918.5, 2849.0, 1747.4, 1461.7, 1428.8, 1376.9, 1297.1, 1266.6, 1252.9, 1229.6, 1203.4, 1185.9, 1175.1, 1096.1, 1059.4, 1018.3, 995.1, 808.0, 728.9, 581.3, 525.8; *m*/*z* (MALDI-TOF) 1328.05 (M^+); δ_H(400 MHz, $CDCl_3$, *J*/Hz) 4.49 (t, 4H, *J* 6.8, CH_2O), 1.84 (tt, 4H, J_1, J_2 6.8, CH_2CH_2O), 1.22–1.49 (m, 60H, CH_2), 0.88 (t, 6H, *J* 6.8, CH_3); δ_C(100 MHz, $CDCl_3$) 163.79 (*C*=O), 145.46, 145.32, 145.25, 144.94, 144.75, 144.73, 144.67, 143.95, 143.15, 143.07, 143.05, 142.27, 141.98, 141.01, 139.05 (C_{60}-sp^2 *C*), 71.68 (C_{60}-sp^3 *C*), 67.46 (CH_2), 52.43 (methano bridge), 31.88, 29.67, 29.64, 29.58, 29.32, 29.20, 28.54, 25.96, 22.64 (CH_2), 14.06 (CH_3).

3: λ_{max}(cyclohexane)/nm 257.5, 325.5, 426.0, 496.0; ν_{max}(KBr)/cm^{-1} 2951.8, 2923.0, 2866.2, 1736.7, 1453.6, 1368.5, 1266.3, 1234.2, 1177.7, 1112.6, 1095.0, 1054.4, 981.7, 946.4, 903.5, 736.7, 702.3, 526.5. *m*/*z* (MALDI-TOF) 1098.80 (M^+); δ_H(400 MHz, $CDCl_3$, *J*/Hz) 5.05 (ddd, 2H, J_1, J_2 11, J_3 4.4, C*H*O), 2.32 (ddd, 2H, J_1 11.6, J_2, J_3 3.2, C*H*H), 2.10 (qqd, 2H, J_1, J_2 7.2, J_3 2.8, C*H*Me$_2$), 1.76 (m, 4H, 2 × C*H*H), 1.61 (m, 4H, 2 × C*H*), 1.22 (ddd, 2H, J_1, J_2, J_3 11, C*H*H), 1.13 (m, 2H, C*H*H), 1.00 (d, 6H, *J* 6, CH_3), 0.92 (d, 6H, *J* 7.2, CH_3), 0.82 (d, 6H, *J* 6.8, CH_3); δ_C(100 MHz, $CDCl_3$) 163.12 (*C*=O), 145.81, 145.43, 145.40, 145.36, 145.24, 145.16, 144.88, 144.79, 144.74, 144.69, 144.55, 143.94, 143.92, 143.13, 143.09, 143.03, 143.02, 142.29, 142.23, 141.94, 141.88, 140.96, 140.94, 138.95 (C_{60}-sp^2 *C*), 78.04 (*C*HO), 71.92 (C_{60}-sp^3 *C*), 53.01 (methano bridge), 46.94 (*C*H), 40.66, 34.10 (CH_2), 31.49, 25.98 (*C*H), 23.08 (CH_2), 22.02, 20.79, 16.01 (CH_3).

6: $\lambda_{max}(CH_2Cl_2)$/nm 245.0, 270.0, 281.0, 318.5, 335.5, 384.5 (sh); ν_{max}(KBr)/cm^{-1} 2956.3, 2918.2, 2850.0, 1736.0, 1469.3, 1396.0, 1378.9, 1351.2, 1265.8, 1242.6, 1215.9, 1164.2, 1073.7, 761.8, 718.3, 530,0; δ_H(400 MHz, $CDCl_3$, *J*/Hz) 4.23 (t, 24H, *J* 6.8, CH_2O), 1.68 (tt, 24H, J_1, J_2 6.8, CH_2CH_2O), 1.17–1.40 (m, 360H, CH_2), 0.88 (t, 36H, *J* 6.8, CH_3); δ_C(100 MHz, $CDCl_3$) 163.97 (*C*=O), 145.83, 141.17, (C_{60}-sp^2 *C*), 69.08 (C_{60}-sp^3 *C*), 66.93 (CH_2), 45.35 (methano bridge), 31.87, 29.70, 29.67, 29.62, 29.54, 29.31, 29.23, 28.39, 25.79, 22.62 (CH_2), 14.03 (CH_3).



Scheme 2 *Reagents and conditions:* i, DMA 10 equiv.; ii, $CH_2(CO_2R)_2$ 10 equiv., CBr_4 10 equiv., DBU 20 equiv., toluene, room temp., 12 h

corresponding conversion with diethyl bromomalonate gives 45% of **1**. Also the direct synthesis of hexaadducts like **5**[4a] and **6**† with an octahedral addition pattern is successful with this modified cyclopropanation reaction when combined with our template activation method (Scheme 2).[4] In these cases 100 mg (0.139 mmol) of C_{60} and 0.286 g (1.39 mmol) of DMA were stirred at room temperature in 60 ml of toluene for 2 h. Then, 0.460 g (1.39 mmol) of CBr_4 and 10 equiv. of malonate were added and 0.414 ml (2.78 mmol) of DBU were added dropwise. After 12 h the crude mixture was purified by flash chromatography. The yields of the hexaadducts **5** and **6** were 48 and 40%, respectively, which is as high as those obtained with the original procedure using *e.g.* diethyl bromomalonate.[4]

Since no adducts derived from the attachment of dibromocarbene to C_{60} are detected and since the reaction gives good yields of monoadducts when only 1.1 mol of DBU per mol of malonate are used, we assume that the mechanism of the reaction involves the formation of the corresponding bromomalonate and subsequent cyclopropanation *via* DBU catalysis.

In conclusion, we have shown that nucleophilic cyclopropanation of C_{60} in high yields is possible starting directly from malonates. This is a significant improvement of the original procedure, since problems associated with the use of bromomalonates are avoided.

Acknowledgements

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