



Diels-Alder Cycloaddition of Substituted Norcaradienes with [60]Fullerene

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Abstract. Substituted norcaradienes, generated by $\text{-Rh}_2(\text{OAc})_4$ catalyzed - cyclopropanation of toluene and benzene with *tert*-butyl diazoacetate, reacts with [60]fullerene to form a new type of fullerene cycloadducts.

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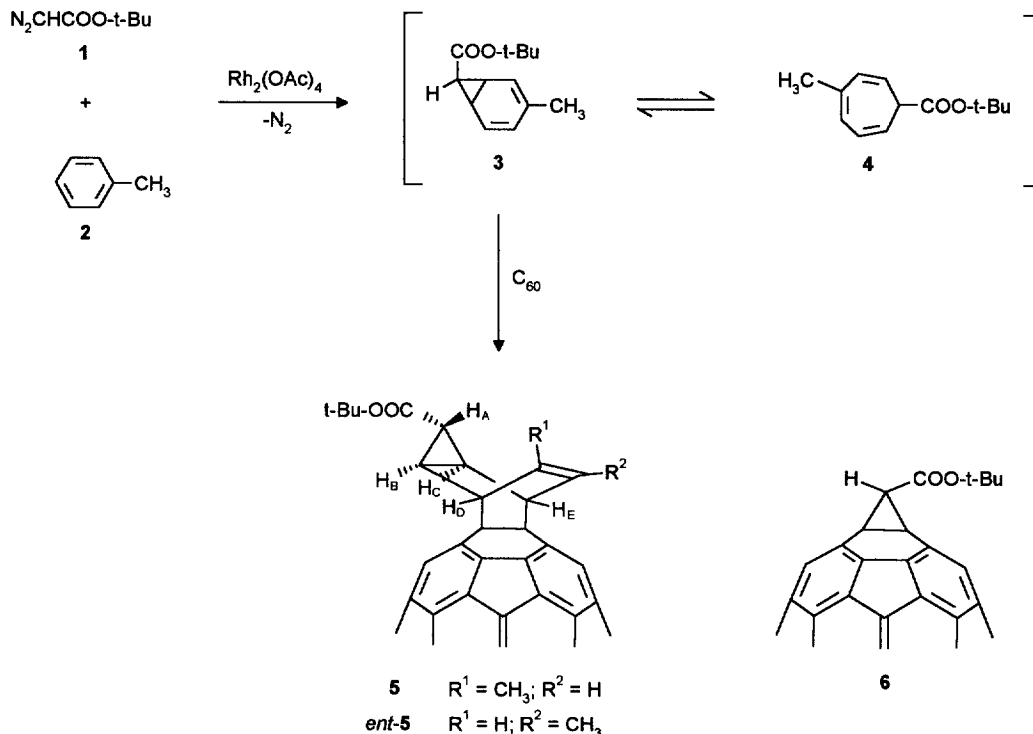
Because of the interesting physical and biological properties of fullerene derivatives, chemical modifications of C_{60} by selective bond formation have been intensively explored, recently.¹⁻³ Cycloaddition reactions provide the most successful method for the functionalization of fullerene.^{4,5} Since the first synthesis of a methanofullerene research in this field has expanded rapidly in many directions.⁶ Several methods are known including the thermal addition of diazo compounds,^{7,8} the reaction with free carbenes,^{9,10} the reaction with ylides,^{11,12} cyclopropanations with stabilized α -halocarbaniones,^{13,14} and the electrosynthesis by the reaction of C_{60} -dianions with dihalocompounds.¹⁵

The cyclopropanation of alkenes with organic diazo compounds can also be achieved by catalytic methods.¹⁶ Catalytic decomposition reactions of diazo compounds are usually carried out in the presence of metals in different oxidation states. We investigated the metal catalyzed reaction of *tert*-butyl diazoacetate with [60]fullerene as a potential new and effective way for the synthesis of methanofullerenes.

In a typical experiment, 200 mg (277.52 μmol) of [60]fullerene and 118 mg (832.56 μmol) of *tert*-butyl diazoacetate were dissolved in dry toluene (150 ml), 10 mg (22.62 μmol) of $\text{Rh}_2(\text{OAc})_4$ was added, and the solution was stirred under argon for 6d. The colour of the solution changed from purple to brown. TLC showed only traces of the expected methanofullerene **6** ($R_f = 0.64$), but a new main product ($R_f = 0.53$; silica gel 60; toluene/n-hexane = 1/1) appeared. Preparative chromatography on silica gel yielded unconverted C_{60} (59 mg), a methanofullerene **6** (6 mg; 4% yield based on converted C_{60}), and the new derivative *5/ent-5* (78 mg; 43% yield based on converted C_{60}).

The ^1H NMR spectrum of *5/ent-5* shows seven signals at 1.53 ppm (s, 9H, *tert*- C_4H_9), 1.82 ppm (t, 1H, H_A), 2.33 ppm (s, 3H, olefinic CH_3), 2.89 ppm (m, 2H, H_B and H_C), 4.30 ppm (m, 1H, H_D for **5**, H_E for *ent-5*), 4.42 ppm (m, 1H, H_E for **5**, H_D for *ent-5*) and 6.55 ppm (d, 1H, olefinic H). The proton decoupled ^{13}C NMR spectrum displays 44 signals of the C_{60} skeleton (42 between 155.89 and 136.32 ppm; two for the sp^3 hybridized carbons at 71.56 and 71.25 ppm). The remaining 11 signals are assigned to the addend.¹⁷ Correlation between the ^1H and ^{13}C atoms allowed the identification of the structure as *5/ent-5* (2D- ^{13}C - ^1H ghmqc and 2D- ^{13}C - ^1H ghsqc investigations on a VARIAN UNITY plus 500 MHz). The UV-VIS absorption

spectrum in toluene shows a strong absorption at 433 nm. This absorption is characteristic of the dihydrofullerene structure, thus indicating that the cycloaddition took place at a junction of two six-membered rings.¹⁸ The IR spectrum exhibits characteristic bands of the fullerene moiety and a C=O absorption at 1710 cm⁻¹. The positive ion FAB mass spectra shows the molecule ion peaks at m/z 927 [M]⁺ (FISONS AUTOSPEC triple sector instrument). All analytical data are in agreement with the proposed structure.



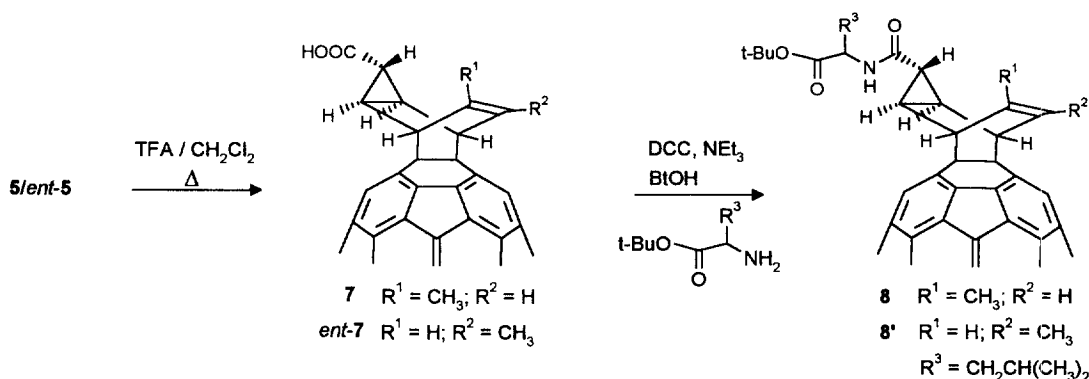
Scheme 1

Scheme 1 describes the cycloaddition of **3** to C₆₀. The Rh₂(OAc)₄ catalyzed cyclopropanation of toluene by **1** yields the norcaradiene **3**. The valence isomerization between the norcaradiene structure **3** and cycloheptatriene **4** is well known. The Diels-Alder reaction in most cases yields norcaradiene-type adducts such as the tricycloadduct *5/ent-5*.¹⁹ In the same manner benzene reacts to the compound **5** in a yield of 24 % (R¹ = R² = H; without optimization). As expected, no reaction is observed using 1,1,2,2-tetrachloroethane as solvent.

Surprisingly, we isolated only one racemic isomer as product of the „domino reaction“. The regioisomer **3** is the main product of the cyclopropanation of toluene by the *tert*-butyl diazoacetate.²⁰ The Diels-Alder cycloaddition leads to an adduct with *anti* cyclopropane orientation relative to the entering dienophile C₆₀. We assume that the bulkiness of the ester group prevents the formation of the *endo*-isomer. Thus, for the cycloadduct *5/ent-5* the configuration *anti/exo* is assigned. This is in agreement with the observed coupling

constant of 2.9 Hz for the *trans* cyclopropane protons H_A and H_B. ¹H NMR studies using the NOE effect prove the *exo* orientation of the ester group. Irradiation of the H_A proton at 1.82 ppm causes the enhancement of the olefinic proton (10%).

The *tert*-butyl group of *5/ent-5* can be removed by TFA. 37 mg (39.92 μmol) of *5/ent-5* were dissolved in 10 ml of dichloromethane and 1 ml TFA. The solution was refluxed for 1 h, the solvent removed under vacuum and the brown solid washed three times with ether to get 32 mg (92% yield) of the free acid *7/ent-7*. We condensed this acid with the leucine *tert*-butyl ester under standard conditions in 80% yield using dicyclohexylcarbodiimide (DCC), hydroxybenzotriazole (BtOH) and triethylamine (Scheme 2). As the splitted signals in the ¹H and ¹³C NMR spectra show, the product **8/8'** is a diastereomeric mixture.²¹



Scheme 2

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17. Selected data for *5/ent-5*: ^1H NMR (500 MHz; CDCl_3 , TMS): δ 6.55 (d, $J = 6.69$ Hz, 1H, olefinic H), 4.42 (m, $J = 4.05$ Hz, $J = 6.69$ Hz, 1H, H_E for **5**, H_D for *ent-5*), 4.30 (m by long range coupling, $J = 3.65$ Hz, 1H, H_D for **5**, H_E for *ent-5*), 2.89 (m, $J = 2.9$ Hz, $J = 3.65$ Hz, $J = 4.05$ Hz, 2H, H_B and H_C), 2.33 (s, 3H, olefinic CH_3), 1.82 (t, $J = 2.9$ Hz, 1H, H_A), 1.53 (s, 9H, *tert*- C_4H_9); ^{13}C NMR (125.70 MHz; CDCl_3 , TMS, $\text{Cr}(\text{acac})_3$): δ 171.48, 155.89, 155.24, 155.17, 154.83, 147.29, 147.32, 146.42, 146.35, 146.22, 146.09, 146.05, 146.01, 145.96, 145.86, 145.68, 145.55, 145.52, 145.43, 145.38, 145.32, 145.21, 144.58, 144.47, 144.33, 143.01, 142.91, 142.86, 142.46, 142.41, 142.27, 142.19, 141.99, 141.77, 141.54, 141.49, 141.44, 140.29, 139.99, 139.93, 139.84, 137.43, 136.35, 136.32, 123.93, 80.34, 71.56, 71.25, 50.09, 44.86, 28.04, 22.22, 21.79, 20.49, 20.07; UV/Vis (toluene): 404, 433, 639, 683, 692, 704; IR (KBr): 2380, 1710, 1510, 1315, 1255, 1180, 765, 530; FAB⁺ (matrix: *o*-nitrophenyl octyl ether): m/z 927 [M]⁺.
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21. Selected data for **8/8'**: ^1H NMR (500 MHz; CDCl_3 , TMS): δ 6.51 - 6.37 (2H), 4.65 (m, 1H), 4.39 (m, 1H), 4.26 (m, 1H), 2.96 (m, 1H), 2.92 (m, 1H), 2.31 (s, 3H), 1.81-1.61 (m, 4H), 1.53 - 1.55 (9H), 1.03 (m, 6H); ^{13}C NMR (125.70 MHz; CDCl_3 , TMS, $\text{Cr}(\text{acac})_3$): δ 172.83, 171.08, 156.26, 155.51, 155.47, 155.08, 147.48, 146.56, 146.49, 146.37, 146.24, 146.20, 146.15, 146.09, 145.87, 145.80, 145.77, 145.59, 145.54, 145.467, 145.42, 145.30, 144.75, 144.64, 144.49, 143.19, 143.00, 142.59, 142.529, 142.44, 142.37, 142.15, 141.94, 141.70, 141.64, 141.53, 140.65, 140.42, 140.08, 140.02, 139.95, 139.90, 137.92, 137.82, 137.78, 136.45, 136.40, 124.20, 124.04, 82.15, 71.84, 71.55, 71.51, 51.54, 50.16, 50.17, 44.86, 44.82, 42.57, 42.48, 28.09, 25.01, 22.88, 22.85, 22.23, 22.21, 22.03, 21.74, 21.57, 21.01, 20.93, 19.87, 19.78.

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