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Dipolar cycloaddition of carbonyl ylides with [60]fullerene: formation of novel heterocycle fused fullerene derivatives

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Abstract—Carbonyl ylides generated by Padwa protocol add to [60]fullerene affording novel heterocycle fused fullerene derivatives in moderate yields. © 2002 Published by Elsevier Science Ltd.

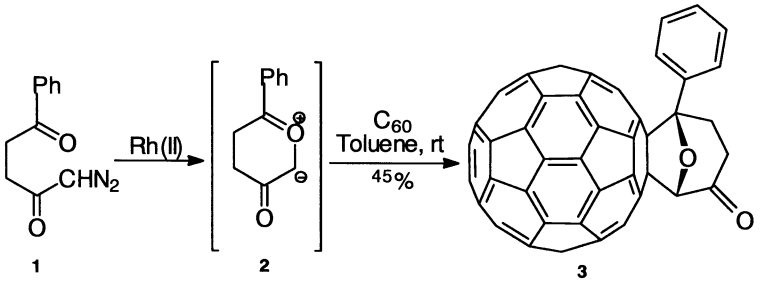
1. Introduction

Since its discovery[1] and isolation in bulk,[2] considerable effort has been made for the exohedral functionalization of [60]fullerene.[3] Synthetic [60]fullerene derivatives find application in materials science[4] as well as in medicinal chemistry.[5] Although a number of synthetic methodologies have been devised, cycloaddition reactions have been found to offer the most versatile routes for the functionalization of [60]fullerene. In cycloaddition reactions, [60]fullerene behaves as an electron deficient alkene. Dipolar cycloaddition reactions[6] and Diels–Alder reactions[7] account for the greatest number of fullerene derivatives reported so far. The reactions of diazocompounds,[8] azides,[9] azomethine ylides,[10] nitrile oxides,[11] mesoionic compounds,[12] pyarazolinium ylides,[13] nitrile imines,[14] nitrile ylides,[15] nitrones,[16] carbonylylide[17] and thiocarbonyl ylide[18] with [60]fullerene have been reported. Carbonyl ylides[19] generated by intramolecular carbenoid–carbonyl cyclization are known to react with acetylenic and olefinic dipolarophiles. Recently in a preliminary report[20] we have shown that six membered cyclic carbonyl ylides undergo facile dipolar cycloaddition with [60]fullerene affording novel organofullerenes. Herein we report details of the extended investigation. It should be noted that there is only an isolated report of the cycloaddition reaction between carbonyl ylide and [60]fullerene.[17]

2. Results and discussion

Our studies were initiated by allowing the diazoketone **1** to react with [60]fullerene in presence of a catalytic amount of $Rh_2(OAc)_4$ in toluene at ambient temperature. The 1,3-dipolar cycloaddition reaction of the carbonyl ylide **2** with [60]fullerene occurred smoothly to afford the product **3** in 45% yield; 86% based on recovered [60]fullerene (Scheme 1).

The product was purified by chromatography on silica gel column and it was characterized by spectroscopic analysis. In the ^1H NMR spectrum of **3** the characteristic signal for the bridgehead proton appeared as a singlet at δ 6.05. In the ^{13}C NMR spectrum, the characteristic sp^3 carbons at the [6,6] junction on the [60]fullerene resonated at δ 75.27



Scheme 1.

Keywords: cycloaddition; carbonyl ylide; [60]fullerene.

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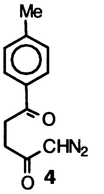
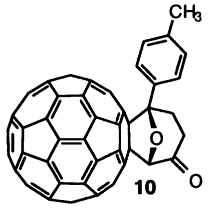
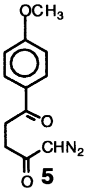
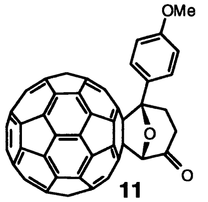
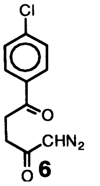
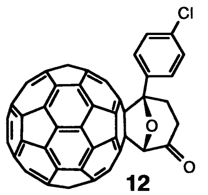
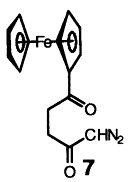
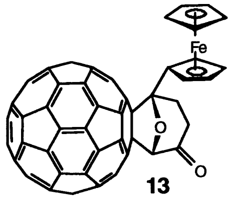
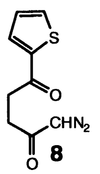
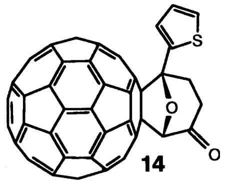
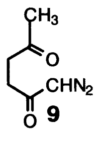
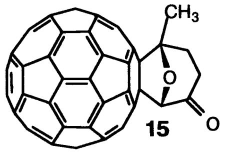
Table 1. Rh(II) catalyzed reaction of diazoketones (**4**–**9**) with [60]fullerene

Diazoketone	Adduct	Yield[a]
 **4**	 **10**	48(87)
 **5**	 **11**	31(43)
 **6**	 **12**	39(79)
 **7**	 **13**	40(85)
 **8**	 **14**	53(82)
 **9**	 **15**	40(87)

[a] Isolated yield (values in paranthesis—based on recovered C_{60}).

and 79.43. The two bridgehead carbons resonated at δ 92.26 and 92.15. The signal at δ 92.15 is due to the bridgehead methine carbon. These assignments were confirmed by DEPT studies. The mass spectrum showing a molecular ion peak at 894 and the HRMS data supported the assigned structure.

The experiment was repeated with different diazoketones (**4**–**9**) and in all cases the reaction proceeded smoothly to afford the cycloadducts (**10**–**15**). The results are summarized in Table 1.

As a follow up to the investigations described above, it was of interest to study the cycloaddition of a five-membered carbonyl ylide[19] **17** with [60]fullerene. Thus when diazoketone **16** was treated with [60]fullerene in presence of Rh(II) acetate, in dry toluene under an atmosphere of argon at ambient temperature, the cycloadduct **18** was obtained in 54% yield. The yield based on recovered [60]fullerene was 92% (Scheme 2).

Somewhat surprisingly, however, the seven-membered carbonyl ylide derived from the diazoketone **19** failed to react with [60]fullerene (Scheme 3).

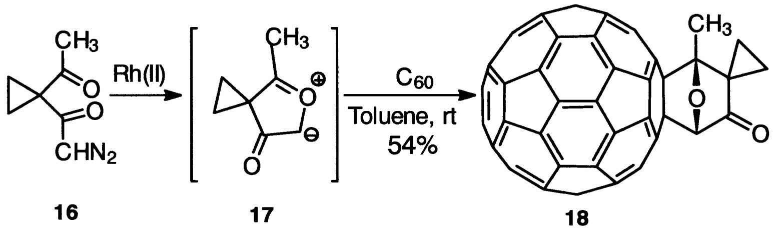
Since [60]fullerene and its derivatives show interesting redox properties,[21] the electrochemical behavior of the cycloadducts **3**, **13** and **14** was studied by cyclic voltametry. Cycloadduct **13** gave a cyclic voltammogram, (Fig. 1), with four reduction waves at potentials shifted to more negative values compared to the parent [60]fullerene. The shift can be attributed to the saturation of a double bond in the cage. This indicates that the electrophilicity of the cycloadduct is less than that of [60]fullerene itself.

The reduction potentials estimated by the position of reduction peaks for compounds **3**, **13** and **14** are given in Table 2 together with those measured for [60]fullerene under identical conditions.

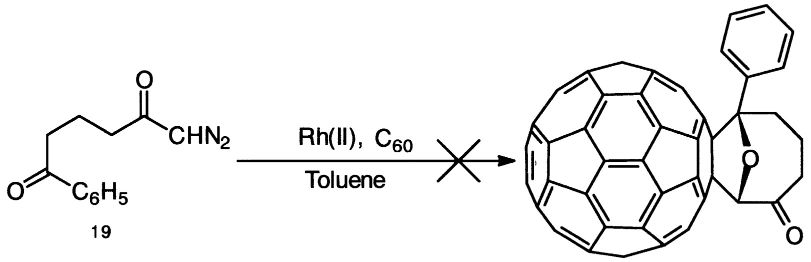
In conclusion, we have found that six and five-membered cyclic carbonyl ylides undergo facile dipolar cycloaddition with [60]fullerene leading to novel derivatives.

3. Experimental

All the reactions were carried out in oven dried glassware under an atmosphere of argon unless otherwise mentioned. The IR spectra were recorded on a Bomem MB series FT-IR spectrophotometer, using potassium bromide pellets. NMR spectra were recorded on Bruker-300 MHz FT-NMR spectrometer using $CDCl_3$–CS_2 (1:2) mixture as solvent for fullerene adducts. The chemical shifts are given in the δ scale with tetramethylsilane as internal standard. High-resolution mass spectra were obtained in EI mode on a



Scheme 2.



Scheme 3.

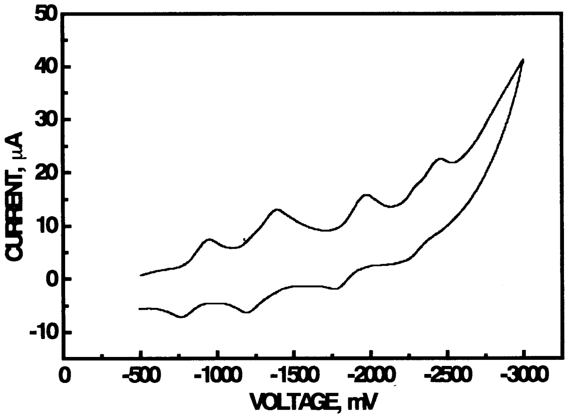


Figure 1.

Table 2. Reduction potential of cycloadducts **3**, **13**, **14** and [60]fullerene

Compound	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4
[60]Fullerene	−0.852	−1.308	−1.799	−2.294
3	−0.932	−1.352	−1.891	−2.394
14	−0.942	−1.381	−1.963	−2.451
13	−0.949	−1.423	−1.993	−2.470

Experimental conditions: V vs Ag^+/Ag; glassy carbon electrode as working electrode; $Bu_4N^+BF_4^-$ (0.1 M) as supporting electrolyte; Scan rate 100 mv/s; toluene–acetonitrile (5:1) as solvent.

Kratos MS50 instrument. Diazoketones (**4**–**8**) were prepared from the corresponding γ-ketoacids by the procedure adopted for the preparation of **1**.[19]

3.1. General procedure for the Rh(II) catalyzed cycloaddition reaction of 1-diazo alkanediones with [60]fullerene

[60]Fullerene was completely dissolved in dry toluene by sonication. To this solution a catalytic amount (0.002 g) of $Rh_2(OAc)_4$ was added and dry, oxygen free argon was passed through it. The diazoketone in toluene, (10–15 mL), taken in a pressure equalizing funnel, was slowly added to the [60]fullerene solution with constant stirring, at the rate of five to six drops in a minute. After the addition was complete, the reaction mixture was allowed to stir for another 30 minutes. The solvent was then removed under reduced pressure and the contents were charged on a silica gel (100–200 mesh) column and eluted with toluene–hexane mixture (1:4). The unreacted [60]fullerene was eluted first and then eluting with toluene–hexane mixture (1:1) afforded the product. The product was dissolved in dry carbon disulfide (2 mL) and dry methanol was added dropwise to it until the product was precipitated completely. The supernatant liquid was decanted off to obtain the product, which was then washed three times with dry methanol and dried in a vacuum oven at 60°C and the product was identified on the basis of its spectral data.

3.1.1. 5′-Phenylbicyclo[3,2,1]-8-oxaoctan-2′-ono[6′,7′;1,2]-[60]fullerene(3). [60]Fullerene (0.036 g, 5×10^{-5} mol) was treated with 1-diazo-5-phenyl-2, 5-pentanedione **1** (0.0101 g, 5×10^{-5} mol) using the general method to afford the product **3** as a black solid (0.0201 g, 45, 86% based on recovered [60]fullerene).

IR ν_{max} (KBr): 3058, 2959, 2859, 1732, 1434, 1215, 1062, 1029, 883, 751, 691, 525 cm^{-1}. δ_H(300 MHz, $CDCl_3$–CS_2) 3.08–3.23 (2H, m, CH_2CH_2CO), 3.62–3.85 (2H, m, CH_2CH_2CO), 6.05 (1H, s, CH_2COCH), 7.28–7.44 (m, 3H, ArH_3), 7.94 (brs, 2H, ArH_2). δ_C (75.4 MHz, $CDCl_3$–CS_2) 33.86, 36.52, 75.27, 79.43, 92.15, 92.26, 125.52, 128.27, 128.66, 134.44, 135.68, 137.15, 139.05, 140.08, 140.25, 140.35, 141.40, 141.58, 141.67, 141.87, 141.90, 142.00, 142.02, 142.18, 142.26, 142.30, 142.61, 142.72, 142.87, 143.03, 143.15, 144.06, 144.24, 144.38, 144.49, 145.00, 145.17, 145.25, 145.43, 145.51, 145.61, 145.71, 145.81, 145.92, 146.05, 146.13, 146.30, 146.41, 146.57, 147.08, 147.18, 149.19, 151.11, 153.26, 153.71, 202.23. DEPT-135: δ 33.86, 36.52: Negative; δ 92.26, 125.52, 128.27, 128.66: Positive. HRMS(EI) Calcd for $C_{71}H_{10}O_2$: 894.0681. Found: 894.0676.

3.1.2. 5′-(4-Methylphenyl)bicyclo[3,2,1]-8-oxaoctan-2′-ono[6′,7′;1,2][60]fullerene (10). [60]Fullerene (0.036 g, 5×10^{-5} mol) was treated with diazoketone **4** (0.011 g, 5×10^{-5} mol) using the general method to afford the product **10** as a black solid (0.022 g, 48, 87% based on recovered [60]fullerene).

IR ν_{max} (KBr): 2955, 2918, 1738, 1438, 1226, 814 cm^{-1}. δ_H (300 MHz $CDCl_3$–CS_2): 2.35 (3H, s, $C_6H_4CH_3$), 3.01–3.26 (2H, m, CH_2CH_2CO), 3.60–3.84 (2H, m, CH_2CH_2CO), 6.03 (1H, s, CH_2COCH), 7.20 (2H, d, J=6.0 Hz, ArH_2), 7.81 (2H, d, J=6.0 Hz, ArH_2). δ_C (75.4 MHz, $CDCl_3$–CS_2) 21.24, 33.67, 36.67, 75.32, 79.57, 92.18, 92.36, 125.48, 129.36, 134.42, 135.75, 137.12, 137.67, 137.91, 138.60, 139.14, 140.09, 140.26, 140.39, 141.40, 141.67, 141.74, 141.84, 141.95, 142.01, 142.07, 142.18, 142.27, 142.37, 142.46, 142.53, 142.72, 142.76, 143.06, 143.18, 144.09, 144.28, 144.43, 144.52, 145.03, 145.18, 145.20, 145.27, 145.40, 145.46, 145.54, 145.59, 145.77, 145.83, 145.94, 146.06, 146.15, 146.32, 146.47, 146.66, 147.11, 147.17, 148.34, 151.30, 153.53, 153.84, 202.32. HRMS(EI) Calcd for $C_{71}H_{10}O_2$: 908. 0837. Found: 908.0805.

3.1.3. 5′-(4-Methoxyphenyl)bicyclo[3,2,1]-8-oxaoctan-2′-ono[6′,7′;1,2][60]fullerene (11). [60]Fullerene (0.072 g, 1×10^{-4} mol) was treated with diazoketone **5** (0.023 g, $1\times^{-4}$ mol) using the general method to afford the product **11** as a black solid (0.021 g, 31, 43% based on recovered [60]fullerene).

IR ν_{max} (KBr): 1725, 1613, 1507, 1248, 1029, 817, 525 cm^{-1}. δ_H (300 MHz $CDCl_3$–CS_2): 3.05–3.21 (2H, m, $\mathit{CH_2}CH_2CO$), 3.59–3.83 (2H, m, $CH_2\mathit{CH_2}CO$), 3.78 (3H, s, $O\mathit{CH_3}$), 6.02 (1H, s, $CH_2CO\mathit{CH}$), 6.90 (2H, d, J=8.5 Hz, $Ar\mathit{H_2}$), 7.84 (2H, d, J=8.5 Hz, $Ar\mathit{H_2}$). δ_C (75.4 MHz, $CDCl_3$–CS_2) 33.59, 36.76, 54.86, 75.14, 78.30, 91.98, 92.05, 113.85, 126.73, 133.58, 134.44, 135.73, 137.02, 137.62, 138.14, 139.17, 140.05, 140.16, 140.30, 141.51, 141.58, 141.90, 141.98, 142.10, 142.14, 142.66, 142.95, 143.12, 143.68, 143.99, 144.18, 144.38, 144.92, 145.08, 145.23, 145.37, 145.42, 145.47, 145.70, 145.86, 146.00, 146.05, 146.22, 146.41, 146.53, 147.02, 148.19, 148.43, 150.53, 151.19, 153.50, 153.76, 159.13, 201.60. HRMS(EI) Calcd for $C_{72}H_{12}O_3$: 924.0786. Found: 924.0775.

3.1.4. 5′-(4-Chorophenyl)bicyclo[3,2,1]-8-oxaoctan-2′-ono[6′,7′;1,2][60]fullerene (12). [60]Fullerene (0.072 g, 1×10^{-4} mol) was treated with diazoketone **6** (0.024 g, 1×10^{-4} mol) using the general method to afford the product **12** as a black solid (0.036 g, 39, 79% based on recovered [60]fullerene).

IR ν_{max} (KBr): 1729, 1419, 1091, 1066, 865 cm^{-1}. δ_H (300 MHz $CDCl_3$–CS_2): 3.06–3.24 (2H, m, $\mathit{CH_2}CH_2CO$), 3.59–3.82 (2H, m, $CH_2\mathit{CH_2}CO$), 6.05 (1H, s, $CH_2CO\mathit{CH}$) 7.40 (2H, d, J=8.6 Hz, $Ar\mathit{H_2}$), 7.90 (2H, brs, $Ar\mathit{H_2}$). δ_C (75.4 MHz, $CDCl_3$–CS_2) 33.63, 36.82, 75.29, 79.30, 91.92, 92.214, 127.06, 128.99, 134.68, 137.35, 137.64, 139.39, 140.13, 140.29, 140.50, 141.54, 141.66, 141.77, 141.81, 141.97, 142.14, 142.28, 142.37, 142.41, 142.78, 142.85, 142.89, 143.15, 143.29, 143.41, 144.41, 144.25, 144.37, 144.51, 144.59, 145.06, 145.10, 145.23, 145.30, 145.38, 145.57, 145.76, 145.89, 145.91, 145.98, 146.05, 146.20, 146.28, 146.42, 147.21, 148.18, 150.89, 152.90, 153.62, 201.17. HRMS(EI) Calcd for $C_{71}H_9O_2Cl$: 928.0291: Found: 928.0283.

3.1.5. 5′-Ferrocenylbicyclo[3,2,1]-8-oxaoctan-2′-ono-[6′,7′;1,2][60]fullerene (13). [60]Fullerene (0.072 g, 1×10^{-4} mol) was treated with diazoketone **7** (0.031 g, 1×10^{-4} mol) using the general method to afford the product **13** as a black solid (0.041 g, 40, 85% based on recovered [60]fullerene).

IR ν_{max} (KBr): 3403, 2925, 2846, 1725, 1593, 1420, 1122, 1023, 811 cm^{-1}. δ_H (300 MHz $CDCl_3$–CS_2): 3.21–3.45 (2H, m, $\mathit{CH_2}CH_2CO$), 3.64–3.81 (2H, m, $CH_2\mathit{CH_2}CO$), 4.21 (m, 2H, $Cp\mathit{H_2}$), 4.33 (m, 1H, $Cp\mathit{H}$), 4.36 (s, 5H, $Cp\mathit{H_5}$), 4.74 (m, 1H, $Cp\mathit{H}$), 5.94 (1H, s, $CH_2CO\mathit{CH}$). δ_C (75.4 MHz, $CDCl_3$–CS_2) 33.32, 35.10, 67.14, 67.79, 68.08, 68.62, 69.29, 75.23, 80.01, 91.42, 91.66, 92.19, 133.74, 135.68, 136.38, 137.53, 139.25, 139.92, 140.02, 140.11, 141.29, 141.44, 141.51, 141.71, 141.79, 141.92, 141.99, 142.01, 142.06, 142.12, 142.42, 142.53, 142.57, 142.87, 142.95, 143.09, 143.95, 144.04, 144.28, 144.35, 144.37, 144.81, 144.88, 144.94, 145.01, 145.07, 145.34, 145.58, 145.64, 145.79, 145.87, 145.92, 146.07, 146.16, 146.34, 146.39, 146.97, 148.33, 151.02, 153.50, 154.09, 202.56. HRMS(EI) Calcd for $C_{75}H_{14}FeO_2$: 1002.0343. Found: 1002.0331.

3.1.6. 5′-Thieneylbicyclo[3,2,1]-8-oxaoctan-2′-ono[6′,7′;1,2][60]fullerene (14). [60]Fullerene (0.050 g, 6.94×10^{-5} mol) was treated with diazoketone **8** (0.015 g, 7.21×10^{-4} mol) using the general method to afford the product **14** as a black solid (0.033 g, 53, 82% based on recovered [60]fullerene).

IR ν_{max} (KBr):1725, 1513, 1420, 890, 698, 525 cm^{-1}. δ_H (300 MHz $CDCl_3$–CS_2): 3.13–3.32 (2H, m, $\mathit{CH_2}CH_2CO$), 3.54–3.61 (1H, m, $CH_2\mathit{CH}(H)CO$), 3.74–3.83 (1H, m, $CH_2CH(\mathit{H})CO$), 5.98 (1H, s, $CH_2CO\mathit{CH}$), 7.02 (1H, dd, J_1=5.0 Hz, J_2=3.6 Hz, $Ar\mathit{H}$), 7.30 (1H, dd, J_1=5.1 Hz, J_2=1.1 Hz, $Ar\mathit{H}$), 7.37 (1H, dd J_1=3.5 Hz, J_2=1.1 Hz, ArH). δ_C (75.4 MHz, $CDCl_3$–CS_2) 33.57, 37.68, 74.78, 79.54, 91.76, 92.17, 124.94, 125.53, 127.09, 134.63, 135.73, 136.97, 137.55, 139.08, 140.11, 140.16, 140.25, 141.31, 141.44, 141.47, 141.52, 141.74, 141.94, 142.10, 142.20, 142.32, 142.63, 142.66, 142.95, 143.09, 143.96, 144.06, 144.13, 144.35, 144.40, 144.54, 144.84, 144.98, 145.04, 145.16, 145.25, 145.38, 145.61, 145.70, 145.84, 145.94, 146.01, 146.10, 146.20, 146.23, 146.30, 146.42, 147.01, 147.08, 147.77, 150.43, 152.56, 153.22, 200.41. HRMS(EI) Calcd for $C_{69}H_8O_2S_1$: 900.0251. Found: 900.0249.

3.1.7. 5′-Methylbicyclo[3,2,1]-8-oxaoctan-2′-ono[6′,7′;1,2][60]fullerene (15). [60]Fullerene (0.072 g, 1×10^{-4} mol) was treated with diazoketone **9** (0.014 g, 1×10^{-4} mol) using the general method to afford the product **15** as a black solid (0.033 g, 40, 87% based on recovered [60]fullerene).

IR ν_{max} (KBr): 2942, 2850, 1732, 1645, 1539, 1501, 1457, 1395, 1220, 864 cm^{-1}. δ_H (300 MHz $CDCl_3$–CS_2): 2.25 (3H, s, $\mathit{CH_3}CCH_2$), 2.88–3.10 (1H, m, $\mathit{CH_2CH}(H)$), 3.50–3.66 (1H, m, $CH_2CH(\mathit{H})$), 5.77 (1H, s, $CH_2CO\mathit{CH}$). δ_C (75.4 MHz, $CDCl_3$–CS_2) 27.23, 33.66, 37.14, 75.62, 78.13, 89.64, 92.16, 134.93, 135.53, 136.77, 137.51, 139.70, 140.17, 140.30, 141.46, 141.58, 141.63, 141.85, 141.89, 141.93, 142.04, 142.05, 142.12, 142.57, 142.64, 142.68, 142.85, 142.95, 143.12, 143.94, 144.14, 144.34, 144.40, 144.43, 144.64, 144.86, 145.04, 145.09, 145.19, 145.36, 145.46, 145.51, 145.62, 145.77, 145.87, 145.95, 146.05, 146.16, 146.34, 146.95, 147.04, 148.62, 151.49, 153.24, 153.49, 201.13. HRMS(EI) Calcd for $C_{66}H_8O_2$: 832.0524; Found: 832.0515.

3.1.8. 4′-Methyl-3′-spirocyclopropanebicyclo[2,2,1]-7-oxoheptan-2′-ono[5′,6′;1,2][60]fullerene (18). [60]Fullerene (0.072 g, 1×10^{-4} mol) was treated with diazoketone **16** (0.015 g, 1×10^{-4} mol) using the general method to afford the product **18** as a black solid (0.045 g, 54, 92% based on recovered [60]fullerene).

IR ν_{max} (KBr): 1745, 1507, 1381, 1016, 824, 525 cm^{-1}. δ_H (300 MHz $CDCl_3$–CS_2): 1.35–1.46 (m, 2H, CH_2CH_2), 1.70–1.74 (m, 1H, CH_2CH(H)), 1.94–1.99 (m, 1H, CH_2CH(*H*)), 2.13 (s, 3H, $OCCH_3$), 5.97 (s, 1H, CO*CH*). δ_C (75.4 MHz, $CDCl_3$–CS_2) 15.56, 15.66, 16.78, 39.40, 74.53, 80.02, 90.58, 93.25, 139.85, 139.89, 139.98, 140.33, 141.53, 141.73, 141.82, 141.89, 141.94, 142.05, 142.18, 142.51, 142.62, 142.65, 142.95, 143.03, 144.06, 144.16, 144.24, 144.54, 144.66, 145.19, 145.25, 145.31, 145.47, 145.51, 145.56, 145.69, 145.80, 145.92, 145.95, 145.98, 146.18, 146.27, 146.95, 147.05, 149.21, 150.40, 151.47, 153.08, 208.24. DEPT-135 16.78, 90.58: Positive; 15.56, 15.66: Negative. HRMS(EI) Calcd for $C_{67}H_8O_2$: 844.0524. Found: 844. 0506.

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