

SHORT
COMMUNICATIONSCatalytic [3+2]-Cycloaddition of Dialkyl, Diallyl, and Dibenzyl Sulfides to Fullerene C₆₀A. R. Tuktarov^a, A. R. Akhmetov^a, M. Pudas^b, A. G. Ibragimov^a, and U. M. Dzhemilev^a^a Institute of Petroleum Chemistry and Catalysis, Russian Academy of Sciences,
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Increased interest in heteroring-fused fullerenes originates from their wide medical and technical applications [1, 2]. A general procedure for the synthesis of fullerenes with fused N,O,S-containing heterorings is based on 1,3-dipolar cycloaddition of ylides generated *in situ* to C₆₀ [3, 4]. For example, bis(trimethylsilylmethyl) sulfoxide in *o*-dichlorobenzene at 110°C gives rise to thiocarbonyl ylide which adds to C₆₀ with formation of dihydrothieno[3',4':1,9](C₆₀-I_h)[5,6]fullerene [3]. Catalytic procedures for the synthesis of dihydrothieno[3',4':1,9](C₆₀-I_h)[5,6]fullerenes have not been reported.

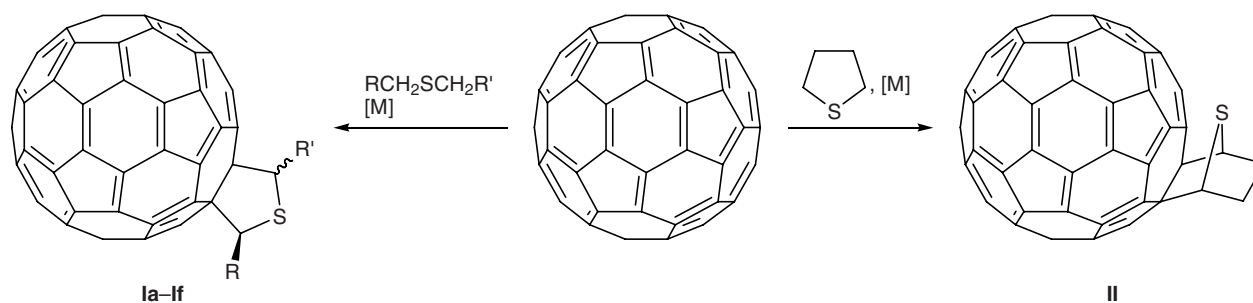
We have developed an effective procedure for the synthesis of difficultly accessible tetrahydrothieno[3',4':1,9](C₆₀-I_h)[5,6]fullerenes by [3+2]-cycloaddition of acyclic and cyclic sulfides to C₆₀ in the presence of cyclopentadiene metal complexes Cp₂TiCl₂, Cp₂ZrCl₂, and Cp₂HfCl₂. The reaction of diethyl sulfide with an equimolar amount of C₆₀ in the presence of 20 mol % of Cp₂MCl₂ (M = Ti, Zr, Hf; toluene, ~150°C, 6 h) gave a ~1:1 mixture of stereoisomeric

2',5'-dimethyl-2',5'-dihydrothieno[3',4':1,9](C₆₀-I_h)[5,6]fullerene (**Ia**) in ~65% yield. Dipropyl, dibutyl, methyl benzyl, dibenzyl, and diallyl sulfides reacted with C₆₀ under analogous conditions to give 60–65% of the corresponding 2',5'-disubstituted derivatives **Ib–If** as mixtures of stereoisomers. The reaction of C₆₀ with tetrahydrothiophene afforded bicyclic ([7]thiabicyclo[2.2.1]heptano)[1',2':1,9](C₆₀-I_h)[5,6]fullerene (**II**) in ~70% yield.

Complexes of other transition metals or their salts [Ni(acac)₂, Pd(acac)₂, Fe(acac)₃, TiCl₄, Cp₂Fe, MnCl₂, CoCl₂, FeCl₃, ZrCl₄] failed to catalyze the reaction; no reaction occurred in the absence of catalyst.

Compound **Ia** displayed a distinct absorption maximum at λ 429 nm in the electronic spectrum, which is typical of closed [6,6]-monoadducts [5, 6]. Its mass spectrum (MALDI TOF) contained the molecular ion peak with *m/z* 808, which is consistent with the assumed structure.

Cycloaddition of dialkyl sulfides to C₆₀ in the presence of Cp₂MCl₂. A finger-like high-pressure



[M] = Ti, Zr, Hf; R = R' = Me (**a**), Et (**b**), Pr (**c**); R = H, R' = Ph (**d**); R = R' = CH₂=CH (**e**), Ph (**f**).

metal reactor was charged with 0.01 mmol of C_{60} , 10 ml of toluene, 0.0105 mmol of the corresponding sulfide, and 0.002 mmol of Cp_2MCl_2 ($M = Ti, Zr, Hf$), and the mixture was heated for 6 h at 150°C under stirring. Products **Ia–If** and **II** were isolated by column chromatography on silica gel L (100–250 μm) using hexane–chloroform (6:1) as eluent.

2',5'-Dimethyl-2',5'-dihydrothieno[3',4':1,9]-(C₆₀-I_h)[5,6]fullerene (Ia) (mixture of stereoisomers, 51:49). IR spectrum, ν , cm^{-1} : 520, 740, 1100, 1380, 1450. UV spectrum: λ_{max} 429 nm. 1H NMR spectrum, δ , ppm: 1.28 d (6H, CH_3), 3.56 q (2H, CH). ^{13}C NMR spectrum, δ_C , ppm: 14.15 (15.41), 65.73 (67.13), 75.05 (77.24), 123–156. Mass spectrum, m/z (I_{rel} , %): 808 $[M]^+$ (3), 777 $[M - 2CH_3]^+$ (3), 720 $[C_{60}]^+$ (100).

2',5'-Diethyl-2',5'-dihydrothieno[3',4':1,9]-(C₆₀-I_h)[5,6]fullerene (Ib) (mixture of stereoisomers, 58:42). IR spectrum, ν , cm^{-1} : 520, 610, 1100, 1380, 1460. UV spectrum: λ_{max} 429 nm. 1H NMR spectrum, δ , ppm: 1.28 d (6H, CH_3), 4.58 q (2H, CH), 1.42 t (4H, CH_2). ^{13}C NMR spectrum, δ_C , ppm: 14.89 (15.43), 24.83 (26.75), 63.25 (65.57), 74.96 (77.79), 123–156. Mass spectrum, m/z (I_{rel} , %): 836 $[M]^+$ (1), 865 $[M + C_2H_5]^+$ (6), 779 $[M - 2C_2H_5 + H]^+$ (49), 720 $[C_{60}]^+$ (100).

2',5'-Dipropyl-2',5'-dihydrothieno[3',4':1,9]-(C₆₀-I_h)[5,6]fullerene (Ic) (mixture of stereoisomers, 61:39). IR spectrum, ν , cm^{-1} : 530, 740, 1100, 1380, 1460. UV spectrum: λ_{max} 428 nm. 1H NMR spectrum, δ , ppm: 0.85 t (6H, CH_3), 1.58–1.68 m (4H, CH_2), 1.73 q (4H, CH_2), 4.36 t (2H, CH). ^{13}C NMR spectrum, δ_C , ppm: 14.26 (15.21), 24.36 (25.67), 37.94 (39.83), 64.07 (65.53), 74.89 (77.25), 123–157.

2'-Phenyl-2',5'-dihydrothieno[3',4':1,9]-(C₆₀-I_h)-[5,6]fullerene (Id). IR spectrum, ν , cm^{-1} : 510, 600, 710, 1090, 1390, 1470. UV spectrum: λ_{max} 428 nm. 1H NMR spectrum, δ , ppm: 3.34 s (2H, CH_2), 4.35 s (1H, CH), 7.05 t (2H, H_{arom}), 7.01 t (1H, H_{arom}), 7.10 d (2H, H_{arom}). ^{13}C NMR spectrum, δ_C , ppm: 56.33, 67.37, 74.89, 125.41, 127.37, 129.06, 145.43, 128–157. Mass spectrum, m/z (I_{rel} , %): 856 $[M]^+$ (1), 779 $[M - Ph]^+$ (25), 720 $[C_{60}]^+$ (100).

2',5'-Divinyl-2',5'-dihydrothieno[3',4':1,9]-(C₆₀-I_h)[5,6]fullerene (Ie). IR spectrum, ν , cm^{-1} : 530, 770, 1100, 1380, 1460. UV spectrum: λ_{max} 427 nm. 1H NMR spectrum, δ , ppm: 4.59 d (4H, CH_2), 5.17 d (2H, CH), 5.84 q (2H, CH). ^{13}C NMR spectrum, δ_C , ppm: 64.74, 77.27, 117.05, 125.74, 128–156.

2',5'-Diphenyl-2',5'-dihydrothieno[3',4':1,9]-(C₆₀-I_h)[5,6]fullerene (If). IR spectrum, ν , cm^{-1} : 520, 740, 1080, 1380, 1440. UV spectrum: λ_{max} 429 nm. 1H NMR spectrum, δ , ppm: 5.13 s (2H, CH), 7.03 t (2H, H_{arom}), 7.00 t (1H, H_{arom}), 7.12 d (2H, H_{arom}). ^{13}C NMR spectrum, δ_C , ppm: 65.36, 74.65, 125.41, 127.37, 129.06, 145.43, 128–156. Mass spectrum, m/z (I_{rel} , %): 932 $[M]^+$ (1), 778 $[M - 2Ph]^+$ (100), 720 $[C_{60}]^+$ (22).

([7]Thiabicyclo[2.2.1]heptano)[3',4':1,9]-(C₆₀-I_h)-[5,6]fullerene (II). IR spectrum, ν , cm^{-1} : 520, 610, 1100, 1380, 1460. UV spectrum: λ_{max} 429 nm. 1H NMR spectrum, δ , ppm: 1.53 q (4H, CH_2), 3.84 t (2H, CH). ^{13}C NMR spectrum, δ_C , ppm: 34.87, 67.38, 75.11, 128–156. Mass spectrum, m/z (I_{rel} , %): 806 $[M]^+$ (1), 779 $[M - CH_2CH_2]^+$ (9), 720 $[C_{60}]^+$ (100).

The products were analyzed by HPLC using an Altex 330 chromatograph (USA) equipped with a UV detector (λ 313 nm). The IR spectra were recorded in KBr on a Specord 75IR spectrometer (Carl Zeiss Jena). The UV spectra were measured on Specord M-40 and Specord M-80 spectrophotometers from solutions in chloroform. The 1H and ^{13}C NMR spectra were obtained on a Bruker AM-300 instrument at 300.13 and 75.46 MHz, respectively, using $CDCl_3$ – CS_2 (1:1) as solvent. The mass spectra were run on a MALDI Voyager-D STR TOF instrument.

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