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Original scientific paper

Radical reactions of xanthates: annulation of the cyclopentene ring

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Abstract: Homoallylic radicals, generated from the corresponding xanthates, react with terminal alkynes to give cyclopentene derivatives in moderate yields.

Keywords: radicals, annulation, cyclopentene, xanthates, alkynes.

In the rich armamentarium of synthetic free radical reactions, the xanthate based methodology occupies a prominent place.[1] An especially useful feature of the radical chemistry of xanthates is the ability of stabilized radicals to add efficiently to non-activated alkenes – a possibility which has given rise to numerous synthetic applications of this method. However, to the best of our knowledge, no examples are known of reactions of xanthate derived radicals with alkynes, although this latter class of compounds should, at least theoretically, be good acceptor partner for group-transfer radical additions.[2] As represented in Scheme 1, radical addition to an alkyne should produce a vinyl radical **1** – a reactive species capable of abstracting the xanthate group from the radical precursor, thus propagating the chain reaction.

To test this possibility, a mixture of xanthate **2** and propargyl acetate was submitted to the "standard" conditions for a radical addition. Indeed, the expected product **3** was formed under both photolytic and thermal initiation; however, the yield was low (17 %) and the conversion incomplete (Scheme 2). Attempts to optimize the reaction conditions did not meet with success. Thus, a synthetically useful xanthate radical addition to alkynes appeared not to be feasible.

Two mechanistic steps could be responsible for this failure: the addition step or the group transfer step. Unable to envisage any reasons hampering the addition step, we believed that it may be a too high reactivity of the intermediary vinyl ra-

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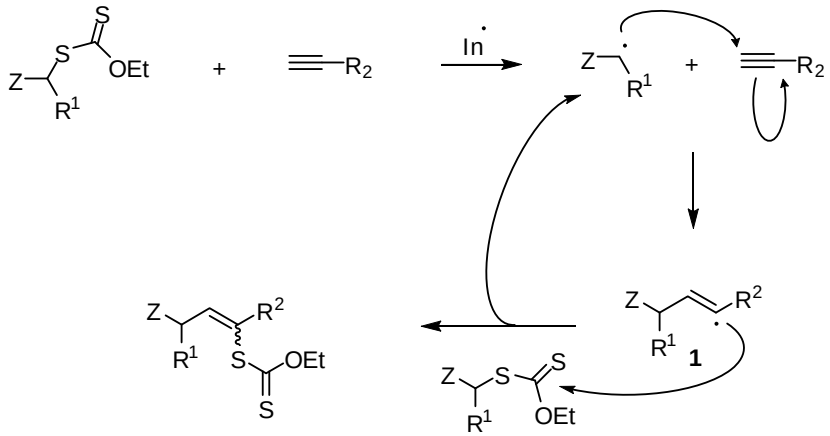
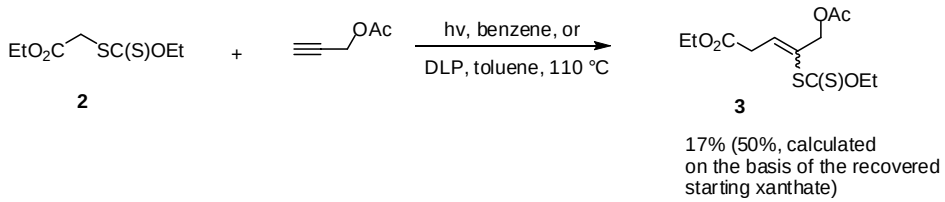
dical **1,** which leads to side reactions and stops the desired radical chain. If this reasoning were correct, the problem could be circumvented by conferring to the vinyl radical another role, instead of a chain carrier. For example, a vinyl radical possessing a Δ^5-olefinic bond could undergo the well-established, rapid 5-*exo*-cyclization; the alkyl radical thus obtained would then effect the crucial chain carrying step, *i.e.*, xanthate group transfer from the radical precursor. This modified reaction is actually a free radical annulation sequence which would produce cyclopentene derivatives.[3] Somewhat counterintuitively, the yield of the sequential reaction as a whole could be better than the yield of the addition step only.



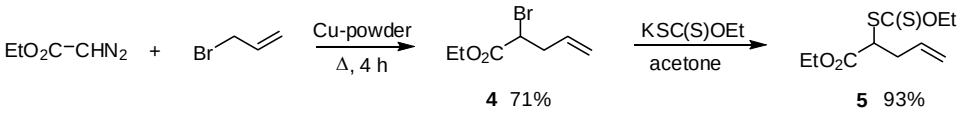
Scheme 1: The proposed mechanism of the intermolecular addition of xanthate derived radicals to alkynes.



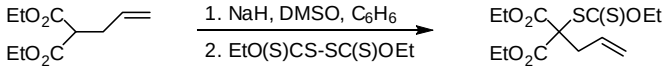
Scheme 2. Addition reaction of a simple xanthate ester to propargyl acetate

To test the correctness of this reasoning and the feasibility of the cyclopentene annulation, suitably substituted xanthate radical precursors **5** and **6**, as shown in Scheme 3, were prepared.[3] Gratifyingly, when a benzene solution of **5** and phenylacetylene was exposed to irradiation with visible light, the desired cyclopentene derivative **7a** was obtained in 33 % yield (42 % yield, calculated on the basis of recovered starting compound **5**). Similarly, other combinations of xanthates and alkynes also gave cyclopentene derivatives **7b**–**g**, in modest to moderate yields, as represented in Scheme 4. Interestingly, with xanthate **5**, the products **7b** and **7c** were obtained stereoselectively, while **7a** was obtained as an equimolar mixture of *cis*/*trans* isomers.

Thus, the intermolecular addition of radicals generated from xanthates to alkynes proved to be possible, provided that the intermediary vinyl radical is trapped by a rapid intramolecular reaction. The described annulation procedure may represent a useful extension of the existing methodology.[4]

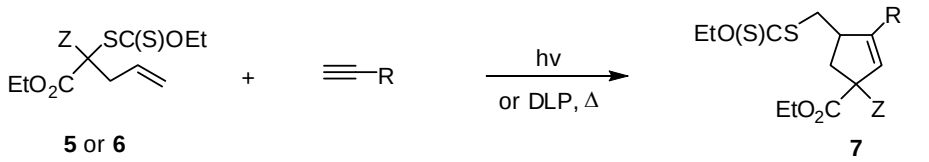


4 71% **5** 93%



6 50%

Scheme 3. Preparation of the annulation precursors.



5 or **6** **7**

Entry	Z	R	method	yield (%)[a]
a	H	Ph	hv	33 (42)
b	H	CH_2OAc	hv	46
c	H	$CH_2O_2CCH_2Cl$	hv	30
d	CO_2Et	n-C_4H_9	hv	60
e	CO_2Et	CH_2OAc	hv	21 (27)
	CO_2Et	CH_2OAc	Δ	30
f	CO_2Et	$CH_2O_2CCH_2Cl$	hv or Δ	30
g	CO_2Et	Ph	hv	48 (62)
	CO_2Et	Ph	Δ	35 (43)

a) Yields in the parenthesis are calculated on the basis of the recovered starting xanthate

Scheme 4. Cyclopentene annulation.

EXPERIMENTAL

General

All chromatographic separations were performed on Silica 10-18, 60Å, ICN Biomedicals. Standard techniques were used for the purification of the reagents and solvents. The NMR spectra were recorded on a Varian Gemini 200, ^{1}H-NMR at 200 MHz, ^{13}C-NMR at 50 MHz, for samples in deuterated chloroform. Chemical shifts are expressed in ppm using tetramethylsilane as the internal standard. The IR spectra were recorded on a Nicolet 6700 FT instrument, and are expressed

in cm^{-1}. The mass spectra were obtained on Agilent Technologies 6210 TOF LC/MS instrument (LC, series 1200).

*Intermolecular addition of radicals to alkynes: ethyl 5-acetoxy-4-(ethoxycarbonothioylthio)pent-3-enoate (**3**)*

In a Pyrex, external water-cooled reactor, a deaerated solution of xanthate **2** (210 mg; 1 mmol) and propargyl acetate (980 mg; 10 mmol) in benzene (1 ml) was irradiated 6 h with a 250 W xenophot sun-lamp, under an argon atmosphere. The solvent was removed under reduced pressure and the product purified by column chromatography on SiO_2 (eluent: 10 % ethyl acetate in petroleum ether) to afford 52 mg (17 %) of the title compound **3,** as a light-yellow oil, and 140 mg of recovered starting xanthate **2** (the yield of **3**, calculated on the basis of the recovered **2**, was 50 %). Spectra of the mixture of isomers: IR_{film}: 2961, 2980, 2920, 2851, 1738, 1647, 1444, 1370, 1224, 1180, 1109 and 1038. ^{1}H-NMR (200 MHz, $CDCl_3$, δ / ppm): 6.61 (*dt*, J_1 = 7.0 Hz, J_2 = 1.0 Hz, 1H, major isomer); 6.47 (*t*, *J* = 7.4 Hz, 1H, minor isomer); 4.86 (*s*, 2H, minor isomer); 4.78 (*d*, *J* = 1.0 Hz, 2H, major isomer); 4.62 (*q*, *J* = 7.0 Hz, 2H); 4.19 (*q*, *J* = 7.2 Hz, 2H, minor isomer); 4.16 (*q*, *J* = = 7.2 Hz, 2H, major isomer); 3.39 (*d*, *J* = 7.0 Hz, 2H, minor isomer); 3.38 (*d*, *J* = 7.0 Hz, 2H, major isomer); 2.10 (*s*, 3H, major isomer); 2.07 (*s*, 3H, minor isomer); 1.4 (*t*, *J* = 7.0 Hz); 1.28 (*t*, *J* = 7.2 Hz, 3H, minor isomer); 1.27 (*t*, *J* = 7.2 Hz, 3H, major isomer). ^{13}C-NMR (50 MHz, $CDCl_3$, δ / ppm): 217.0, 170.4, 170.2, 139.8, 136.1, 129.3, 70.6, 70.3, 66.8, 62.0, 61.1, 35.2, 34.7, 20.8, 14.1, 13.6.

*Ethyl 2-bromo-4-pentenoate (**4**)*[3,5]

A suspension of copper powder (50 mg; 0.78 mmol) in allyl bromide (23 g; 0.19 mol) was heated gently to reflux. To this mixture was added dropwise over 4 h a solution of allyl bromide (3 ml) in ethyl diazoacetate (3 g; 26 mmol). When the addition was complete, the mixture was refluxed for a further 60 min, then filtered, concentrated and distilled under reduced pressure, to give 3.83 g (71 %) of the title compound **4**, E_{21} 88–90 °C; the physical data were identical to that previously reported.[5]

S-*(1-Ethoxycarbonyl-3-butenyl)-O-ethyl dithiocarbonate (**5**)*[3]

A solution of **4** (18 mmol) in acetone (2 ml) was added to a suspension of potassium *O*-ethyl xanthate (2.9 g; 18 mmol) in acetone (5 ml), over 10 min, with stirring under an argon atmosphere. Upon completion of the reaction, the acetone was removed under reduced pressure and the residue was partitioned between water and ether. The combined ethereal extract was dried over anh. sodium sulfate and concentrated to give 4.04 g (93 %) of the title compound **5** as a light-yellow oil. ^{1}H-NMR (δ, ppm): 5.89–5.68 (*m*, 1H); 5.21–5.09 (*m*, 2H); 4.64 (*q*, *J* = 7.0, 2H); 4.43 (*t*, *J* = 7.0 Hz, 1H); 4.21 (*q*, *J* = 7.2 Hz, 2H); 2.76–2.60 (*m*, 2H); 1.42 (*t*, *J* = 7.2 Hz, 3H); 1.30 (*t*, *J* = 7.0 Hz, 3H). IR_{film} (ν, cm^{-1}): 3081, 2982, 1737, 1642, 1293.

S-*(1,1-Bisethoxycarbonyl-3-butenyl)*-O-*ethyl dithiocarbonate (**6**)*[3]

Sodium hydride (80 % in mineral oil) was added to a solution of diethyl allylmalonate (2.0 g; 10 mmol) in benzene (90 ml) and DMSO (10 ml), and the mixture was stirred until a clear solution was formed. To this solution, diethyl dithiobis(thioformate) (2.66 g; 11 mmol) was added and the reaction mixture was stirred at r.t. Upon completion of the reaction, the mixture was carefully diluted with water and extracted with benzene. The combined organic extract was washed with water, dried over anh. sodium sulfate and concentrated under reduced pressure. Purification by column chromatography (SiO_2; eluent: petroleum ether/ethyl acetate 95/5) afforded 1.6 g (50 %) of the title compound **6** as a light-yellow oil. ^{1}H-NMR (δ, ppm): 5.95–5.75 (*m*, 1H); 5.20–5.08 (*m*, 2H); 4.60 (*q*, *J* = 7.1 Hz, 2H); 4.24 (*q*, *J* = 7.2 Hz, 4H); 3.14–3.06 (*m*, 2H); 1.39 (*t*, *J* = 7.1 Hz, 3H); 1.27 (*t*, *J* = 7.2 Hz, 6H). ^{13}C-NMR (δ, ppm): 209.2; 166.5; 131.6; 119.8; 70.0; 66.6; 62.5; 39.3; 13.8; 13.0. IR_{film} (ν, cm^{-1}): 3080, 2983, 1736, 1642, 1294, 1228, 1132.

*General procedure for the annulation reaction with photolytic initiation: diethyl 3-butyl-4-((ethoxycarbonothioylthio)methyl)cyclopent-2-ene-1,1-dicarboxylate (**7d**)*

In a Pyrex, external water-cooled reactor, a deaerated solution of xanthate **6** (100 mg; 0.3 mmol) and 1-hexyne (246 mg; 3 mmol) in benzene (0.3 ml) was irradiated 3 h with a 250 W xenophot sun lamp, under an argon atmosphere. The solvent was removed under reduced pressure and the product purified by column chromatography on SiO_2 (eluent: 5 % ethyl acetate in petroleum ether) to afford 75 mg (60 %) of the title compound **7d** as a light-yellow oil. IR_{film} (ν, cm^{-1}): 2959, 2931, 2871, 1732, 1645, 1462, 1367, 1232, 1112, 1050. ^{1}H-NMR (200 MHz, $CDCl_3$) (δ, ppm): 5.55 (*d*, J = 1.4 Hz, 1H); 4.65 (*q*, J = 7.0 Hz, 2H); 4.31–4.11 (*m*, 4H); 3.56 (*dd*, J_1 = 13.2 Hz, J_2 = 3.8 Hz, 1H); 3.18–2.97 (*m*, 1H); 2.90 (*dd*, J_1 = 13.0 Hz, J_2 = 9.6 Hz, 1H); 2.72 (*dd*, J_1 = 13.8 Hz, J_2 = 8.0 Hz, 1H); 2.25–2.04 (*m*, 3H) 1.43 (*t*, J = 7.0 Hz, 3H); 1.36–1.21 (*m*, 10H); 0.92 (*t*, J = 7.0 Hz, 3H). ^{13}C-NMR (50 MHz, $CDCl_3$) (δ, ppm): 214.7 (C); 171.4 (C); 171.2 (C); 151.1 (C); 123.4 (CH); 69.9 (CH_2); 64.8 (C); 61.4 (CH_2); 45.2 (CH); 39.7 (CH_2); 37.3 (CH_2); 29.3 (CH_2); 28.6 (CH_2); 22.3 (CH_2); 13.9 (CH_3); 13,8 (CH_3); 13.7 (CH_3). HRMS (EI): calcd. for $C_{19}H_{31}O_5S_2$ ($M+H^+$) 403.1607; found 403.1591.

*General procedure for the annulation reaction with thermal initiation: diethyl 3-((2-chloroacetoxy)methyl)-4-((ethoxycarbonothioylthio)methyl)cyclopent-2-ene-1,1-dicarboxylate (**7f**)*

A deaerated solution of xanthate **6** (100 mg; 0.3 mmol) and propargyl chloroacetate (400 mg; 3 mmol) in benzene (0.3 ml) was heated to reflux under an argon atmosphere, while dilauroyl peroxide (4 mg) was added every 2 h. After 5 h, the reaction was complete (TLC). The mixture was concentrated under reduced pressure and purified by column chromatography on SiO_2 (eluent: 10 % ethyl acetate in petroleum ether) to afford 43 mg (30 %) of the title compound **7f** as a light-yellow oil. IR_{film} (ν, cm^{-1}): 2982, 2938, 1731, 1446, 1367, 1235, 1163, 1048. ^{1}H-NMR (200 MHz, $CDCl_3$) (δ, ppm): 5.80 (*s*, 1H); 4.84 (*s*, 2H); 4.62 (*q*, J = 7.3 Hz, 2H); 4.29–4.14 (*m*, 4H) 4.13 (*s*, 2H); 3.53 (*dd*, J_1 = 13.5 Hz, J_2 = 4.2 Hz , 1H); 3.33–3,22 (*m*, 2H); 3.02 (*dd*, J_1 = 13.2 Hz, J_2 = 9.0 Hz , 1H); 2,78 (*dd*, J_1 = 14.0 Hz, J_2 = 8.4 Hz , 1H); 2.31 (*dd*, J_1 = 14.0 Hz, J_2 = 5.1 Hz, 1H); 1.43 (*t*, J = 7.0 Hz, 3H); 1.26 (*t*, J = 7.2 Hz, 3H); 1.26 (*t*, J = 7.0 Hz, 3H). ^{13}C-NMR (50 MHz, $CDCl_3$) (δ, ppm): 214.3 (C); 170.5 (C); 170.3 (C); 166.8 (C); 143.9 (C); 128.6 (CH); 70.2 (CH_2); 65.0 (C); 62.6 (CH_2); 61.8 (CH_2); 44.1 (CH); 40.7 (CH_2); 39.4 (CH_2); 37.4 (CH_2); 13.9 (2 x CH_3); 13.7 (CH_3). HRMS (EI): calcd. for $C_{18}H_{26}O_7S_2Cl$ ($M+H^+$) 453.0803; found 453.0804.

Spectral data for the other annulated compounds

Ethyl 4-((ethoxycarbonothioylthio)methyl)-3-phenylcyclopent-2-enecarboxylate (**7a**): IR_{film} (ν, cm^{-1}): 3057, 2957, 2924, 2854, 1730, 1646, 1445, 1215, 1112, and 1049. ^{1}H-NMR (200 MHz, $CDCl_3$) (δ, ppm): 7.57–7.46 (*m*, 2H); 7.41 (*m*, 3H); 6.15–6.14 (*m*, 1H, isomer A); 6.09–6.07 (*m*, 1H, isomer B); 4.71–4.58 (*m*, 2H), 4.65 (*q*, J = 7.0 Hz, 2H, isomer A); 4.64 (*q*, J = 7.0 Hz, 2H isomer B); 3.79–3.55 (*m*, 3H); 2.98–2.80 (*m*, 1H); 2.60–2.45 (*m*, 1H); 2.29–2.14 (*m*, 1H); 1.43 (*t*, J = 7.0 Hz, 3H, isomer A); 1.40 (*t*, J = 7.2 Hz, 3H, isomer B); 1.29 (*t*, J = 7.2 Hz, 3H, isomer A); 1.27 (*t*, J = 7.0 Hz, 3H, isomer B). ^{13}C-NMR (50 MHz, $CDCl_3$) (δ, ppm): 214.0, 174.0, 147.4, 134.5, 128.5, 127.9, 126.7, 126.4, 125.7, 125.5, 70.0, 69.9, 60.8, 49.4, 43.9, 40.4, 39.60, 32.5, 32.1, 14.2, 13.8, 11.4. HRMS (EI): calcd. for $C_{18}H_{23}O_3S_2$ ($M+H^+$) 351.1083; found 351.1083.

Ethyl 3-(acetoxymethyl)-4-((ethoxycarbonothioylthio)methyl)cyclopent-2-enecarboxylate (**7b**): IR_{film} (ν, cm^{-1}): 2981, 2932, 1738, 1652, 1450, 1369, 1227, 1112, and 1050. ^{1}H-NMR (200 MHz, $CDCl_3$) (δ, ppm): 5.81 (*s*, 1H); 4.71 (*s*, 2H); 4.65 (*q*, J = 7.2 Hz, 2H); 4.15 (*q*, J = 7.2 Hz, 2H); 3.64–3.49 (*m*, 2H); 3.15–2.97 (*m*, 2H); 2.54–2.38 (*m*, 1H); 2.11(*s*, 3H); 2.10–1.97 (*m*, 1H); 1.43 (*t*, J = 7.0 Hz, 3H); 1.27 (*t*, J = 7.2 Hz, 3H). ^{13}C-NMR (50 MHz, $CDCl_3$) (δ, ppm): 214.7 (C); 173.8 (C); 170.7 (C); 142.8 (C); 128.6 (CH); 70.0 (CH_2); 61.3 (CH_2); 60.9 (CH_2); 49.0 (CH); 44.3 (CH); 39.9 (CH); 32.9 (CH); 20.9 (CH_3); 14.2 (CH_3); 13.8 (CH_3). HRMS (EI): calcd. for $C_{15}H_{23}O_5S_2$ ($M+H^+$) 347.0981; found 347.0989.

Ethyl 3-((2-chloroacetoxy)methyl)-4-((ethoxycarbonothioylthio)methyl)cyclopent-2-enecarboxylate (**7c**): IR_{film} (ν, cm^{-1}): 2984, 1731, 1448, 1371, 1286, 1216, 1113, and 1050. ^{1}H-NMR (200 MHz, $CDCl_3$) (δ, ppm): 5.86 (*s*, 1H); 4.84 (*s*, 2H); 4.65 (*q*, *J* = 7.0 Hz, 2H); 4.15 (*q*, *J* = 7.1 Hz, 2H); 4.12 (*s*, 2H); 3.59–3.49 (*m*, 2H); 3.11–2.99 (*m*, 2H); 2.55–2.31 (*m*, 1H); 2.17–1.97 (*m*, 1H); 1.43 (*t*, *J* = 7.0 Hz, 3H); 1.26 (*t*, *J* = 7.1 Hz, 3H). ^{13}C-NMR (50 MHz, $CDCl_3$) (δ, ppm): 214.5 (C); 173.5(C); 166.9 (C); 141.8 (C); 129.4 (CH); 70.1 (CH_2); 62.8 (CH_2); 60.9 (CH_2); 48.9 (CH); 44.2 (CH); 40.7 (CH_2); 39.7 (CH_2); 32.9 (CH_2); 14.1 (CH_3); 13.7 (CH_3).

Diethyl 3-(acetoxymethyl)-4-((ethoxycarbonothioylthio)methyl)cyclopent-2-ene-1,1-dicarboxylate (**7e**): IR_{film} (ν, cm^{-1}): 2982, 2936, 1732, 1445, 1367, 1223, 1112, and 1047. ^{1}H- NMR (200 MHz, $CDCl_3$) (δ, ppm): 5.87 (*d*, *J* = 1.6 Hz, 1H); 4.72 (*s*, 2H); 4.65 (*q*, *J* = 7.0 Hz), 4.32–4.11 (*m*, 4H); 3.55 (*dd*, J_1 = 13.2 Hz, J_2 = 4.0 Hz, 1H); 3.29–3.21 (*m*, 1H); 3.00 (*dd*, J_1 = 13.2 Hz, J_2 = 9.2 Hz, 1H); 2.78 (*dd*, J_1 = 14.0 Hz, J_2 = 8.4 Hz, 1H); 2.31 (*dd*, J_1 = 14.0 Hz, J_2 = 5.0 Hz, 1H); 2.12 (*s*, 3H); 1.43 (*t*, *J* = 7.0 Hz, 3H); 1.26 (*t*, *J* = 7.2 Hz, 3H); 1.25 (*t*, *J* = 7.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) (δ, ppm): 214.4 (C); 170.7 (C); 170.5 (C); 144.8 (C); 127.6 (CH); 70.1 (CH_2); 65.0 (C); 61.8 (CH_2); 61.1 (CH_2); 44.1 (CH); 39.4 (CH_2); 37.4 (CH_2); 20.9 (CH_3); 14.0 (CH_3); 13.7 (CH_3). HRMS (EI): calcd. for $C_{18}H_{26}O_7S_2Na$ ($M+Na^+$) 441.1012; found 441.0992.

Ethyl 4-((ethoxycarbonothioylthio)methyl)-3-phenylcyclopent-2-enecarboxylate (**7g**): Spectra of the mixture of isomers: IR_{film} (δ, ppm): 3057, 2957, 2924, 2854, 1730, 1646, 1445, 1215, 1112, 1049. ^{1}H-NMR (200 MHz, $CDCl_3$) (δ, ppm): 7.57–7.46 (*m*, 2H); 7.41 (*m*, 3H); 6.15–6.14 (*m*, 1H, isomer A); 6.09–6.07 (*m*, 1H, isomer B); 4.71–4.58 (*m*, 2H), 4.65 (*q*, *J* = 7.0 Hz, 2H, isomer A); 4.64 (*q*, *J* = 7.0 Hz, 2H, isomer B); 3.79–3.55 (*m*, 3H); 2.98–2.80 (*m*, 1H); 2.60–2.45 (*m*, 1H); 2.29–2.14 (*m*, 1H); 1.43 (*t*, *J* = 7.0 Hz, 3H, isomer A); 1.40 (*t*, *J* = 7.2 Hz, 3H, isomer B); 1.29 (*t*, *J*= = 7.2 Hz, 3H, isomer A); 1.27 (*t*, *J* = 7.0 Hz, 3H, isomer B). ^{13}C-NMR (50 MHz, $CDCl_3$) (δ, ppm): 214.0, 174.0, 147.4, 134.5 128.5, 127.9, 126.7, 126.4, 125.7, 125.5, 70.0, 69.9, 60.83, 49.4, 43.9, 40.4, 39.60, 32.5, 32.1, 14.2, 13.8, 11.4. HRMS (EI): calcd. for $C_{18}H_{23}O_3S_2$ ($M+H^+$) 351.1083; found 351.1083.

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И З В О Д

РАДИКАЛСКЕ РЕАКЦИЈЕ КСАНТАТА: АНЕЛАЦИЈА ЦИКЛОПЕНТЕНОВОГ ПРСТЕНА

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Хомоалилни радикали, настали из одговарајућих ксантата, реагују са терминалним алкинима и дају деривате циклопентена у умереним приносима.

(Примљено 3. јула 2007)

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2. In reference 1b) (page 207) an example of addition to phenylacetylene is provided. However, no reference to the primary literature was given, and we experienced difficulties in trying to repeat the result reported (64 % yield of the addition product)
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