Synthesis and transformations of metallocycles
14.* Stereoselective synthesis of *trans*-3,4-dialkyltetrahydrothiophenes

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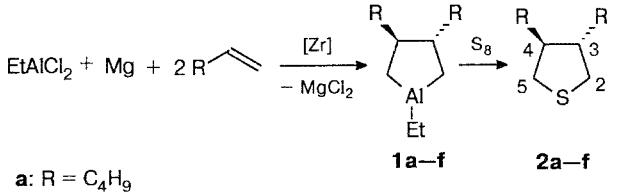
A one-pot stereoselective method was developed for the synthesis of *trans*-3,4-dialkyltetrahydrothiophenes from α-olefins, $EtAlCl_2$, metallic magnesium, and elementary sulfur (S_8) in the presence of catalytic amounts of Cp_2ZrCl_2.

Key words: *trans*-3,4-disubstituted tetrahydrothiophenes, synthesis.

Recently, we performed the transformations of 3-alkylsubstituted alumacyclopentanes (ACP)[2,3] to alkyl-substituted tetrahydrothiophenes, selenophenes,[4] cyclobutanes,[5] and 1,1-dialkylcyclopropanes.[6]

In a continuation of the study of ACP, the present work showed that ACP **1a—f**, like monosubstituted ACP, react fairly readily with elemental sulfur, which is not typical of trialkylalanes.[8] A new stereoselective method for synthesizing *trans*-3,4-dialkyltetrahydrothiophenes **2a—f** from dialkyl-ACP and elementary sulfur was found. Alumacyclopentanes were obtained from α-olefins, $EtAlCl_2$, and Mg in the presence of 3—5 mol. % Cp_2ZrCl_2 or $ZrCl_4$ (*cf.* Ref. 7). When ACP **1a—f** were heated with elemental sulfur in benzene (6—8 h at 80 °C) in a ratio S_8 : $EtAlCl_2$ = 3 : 1, compounds **2a—f** were obtained in 65—80 % yields.



1a—f **2a—f**

a: R = C_4H_9

b: R = C_5H_{11}

c: R = C_6H_{13}

d: R = $(CH_3)_2CH(CH_2)_2$

e: R = $PhCH_2$

f: R = 3-cyclohexenyl

The structures of **2a—f** were confirmed by their ^1H and ^{13}C NMR spectra. The parameters of the ^{13}C spectra for compounds **2a—f** with respect to the effect of the two alkyl substituents were evaluated by comparing them with the spectra of unsubstituted tetrahydrothiophene and 3-alkyltetrahydrothiophenes.[4,9,10] The similarity of the chemical shifts of the vicinal methylene C(3) and C(3′) carbon atoms in compounds **2a—f** and the methylene C(3) carbon atoms in β-alkyltetrahydrothiophenes indicates that the steric 1,2-*cis*-interaction of the alkyl substituents causing strong diamagnetic shifts[1] is absent, which confirms the *trans*-orientation (*ee*) of the 3,4-substituents. Furthermore, the difference in the chemical shifts for the pseudoaxial and pseudoequatorial protons of the S—CH_2 groups in compound **2e**, which is observable at +25 °C, implies the *trans*-orientation of the substituents, since in the case of *cis* isomers, this difference is much smaller.[11,12]

The results obtained indicate that the cycloalumination of α-olefins with $EtAlCl_2$ and Mg in the presence of catalytic amounts of Cp_2ZrCl_2 followed by the *in situ* reaction of the formed 3,4-disubstituted ACP with S_8 affords *trans*-3,4-disubstituted tetrahydrothiophenes in high yields and with high selectivity.

Experimental

TLC was performed on Silufol. GLC was performed on a Khrom-5 chromatograph using He as the carrier gas, 1200×3 mm column, 5 % SE-30 or 15 % PEG-6000 on Chromaton N-AW. IR spectra were recorded in films on a UR-20 spectrophotometer. Mass spectra were obtained on an MX-1300 spectrometer, energy of ionizing electrons 70 and 12 eV, temperature of the feed vessel 100 °C. ^1H NMR spectra were recorded in $CDCl_3$ on a Tesla BS-567 spectrometer (100 MHz). ^{13}C NMR spectra were obtained in C_6D_6 on a Jeol-90Q spectrometer (22.5 MHz) using TMS as the internal standard.

Synthesis of *trans*-3,4-dialkyltetrahydrothiophenes. Dry benzene (35—40 mL) was added under argon to dialkyl-ACP **1a—f** (10 mmol) (*cf.* Ref. 7), then S_8 (powder) was added in small portions. The temperature was increased to ~80 °C, and the mixture was stirred for 6—8 h. Then the mixture was

* For part 13, see Ref. 1.

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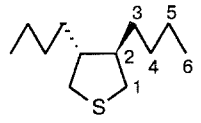
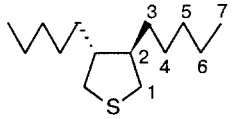
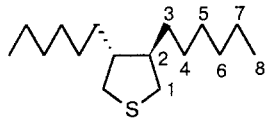
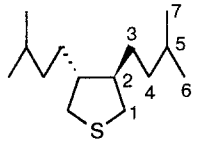
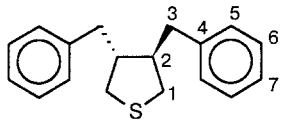
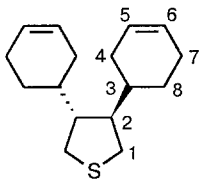
Table 1. Chemical shifts (δ), coupling constants ($^1J_{C,H}$/Hz), and multiplicity of signals in the ^{13}C NMR spectra of disubstituted tetrahydrothiophenes

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
2a 	36.53 t	48.76 d	32.75 t	30.25 t	22.93 t	14.01 q		
2b 	36.45 t	48.76 d	32.94 t	27.70 t	32.12 t	22.63 t	14.04 q	
2c 	36.42 t (142.65)	48.36 d (127.95)	33.10 t (125.48)	20.09 t (123.54)	29.64 t (125.51)	31.92 t (125.30)	22.71 t	14.12 q
2d 	36.54 t (140.05)	48.96 d (127.0)	30.76 t (122.6)	37.26 t (122.80)	28.27 d (125.9)	22.38 q (124.42)	22.88 q (123.24)	
2e 	35.43 t (142.18)	49.28 d (128.08)	38.17 t (126.0)	140.10 c	128.74 d	128.34 d	125.71 d	
2f 	34.16 t	49.07 d	38.70 d	32.12 t	126.52 d	127.13 d	25.75 t	30.86 t

treated with 5 % HCl and extracted with ether. Individual products were isolated by distillation *in vacuo* or by column chromatography (silica gel L, 40/100 μ, hexane—ether, 9:1). The purity of the products was 95—98 %.

***trans*-3,4-Dibutyltetrahydrothiophene (2a).** Yield 80 %. R_f 0.50. IR, ν/cm^{-1}: 2970, 2940, 2870, 1465, 1270, 1080. ^1H NMR, δ: 0.90 (t, 6 H, CH_3); 1.10—1.88 (m, 14 H, CH, CH_2); 2.38—2.60, 2.88—3.08 (m, 4 H, CH_2S). MS, *m/z*: 200 [M$^+$]. Found (%): C, 72.12; H, 12.00; S, 15.88. $C_{12}H_{24}S$. Calculated (%): C, 72.00; H, 12.00; S, 16.00.

***trans*-3,4-Dipentyltetrahydrothiophene (2b).** Yield 78 %. R_f 0.52. IR, ν/cm^{-1}: 2975, 2950, 2870, 1470, 1120, 920, 750. ^1H NMR, δ: 0.89 (t, 6 H, CH_3); 1.10—1.80 (m, 18 H, CH, CH_2); 2.37—2.62, 2.82—3.10 (m, 4 H, CH_2S). MS, *m/z*: 228 [M$^+$]. Found (%): C, 73.61; H, 12.25; S, 14.14. $C_{14}H_{28}S$. Calculated (%): C, 73.68; H, 12.28; S, 14.04.

***trans*-3,4-Dihexyltetrahydrothiophene (2c).** Yield 77 %. R_f 0.54. IR, ν/cm^{-1}: 2970, 2940, 2870, 1470, 745. ^1H NMR, δ: 0.86 (t, 6 H, CH_3); 1.08—1.86 (m, 22 H, CH, CH_2); 2.40—2.58, 2.86—3.04 (m, 4 H, CH_2S). MS, *m/z*: 256 [M$^+$]. Found (%): C, 75.08; H, 12.54; S, 12.38. $C_{16}H_{32}S$. Calculated (%): C, 75.00; H, 12.50; S, 12.50.

***trans*-3,4-Diisopentyltetrahydrothiophene (2d).** Yield 72 %. R_f 0.51. IR, ν/cm^{-1}: 2970, 2935, 2860, 1470, 1390, 1370, 1230, 1210, 1180, 750. ^1H NMR, δ: 0.88 (d, 12 H, CH_3); 1.07—1.76 (m, 12 H, CH, CH_2); 2.35—2.98 (m, 4 H, CH_2S). MS, *m/z*: 228 [M$^+$]. Found (%): C, 73.61; H, 12.34; S, 14.05. $C_{14}H_{28}S$. Calculated (%): C, 73.68; H, 12.28; S, 14.04.

***trans*-3,4-Dibenzyltetrahydrothiophene (2e).** Yield 65 %. R_f 0.46. IR, ν/cm^{-1}: 3100, 3080, 3040, 2940, 2870, 1605, 1500, 1460, 1130, 760, 720. ^1H NMR, δ: 2.53, 2.87 (both d d, $^2J_{HH}$ = −13.37 Hz, 2 H + 2 H, CH_2S); 2.20—2.33 (m, 2 H, CH); 2.62, 2.82 (both d d, $^2J_{H,H}$ = −10.07 Hz, 2 H + 2 H, CH_2Ph). MS, *m/z*: 268 [M$^+$]. Found (%): C, 80.48; H, 7.52; S, 12.00. $C_{18}H_{20}S$. Calculated (%): C, 80.60; H, 7.46; S, 11.94.

***trans*-3,4-Di(3-cyclohexenyl)tetrahydrothiophene (2f).** Yield 69 %. R_f 0.52. IR, ν/cm^{-1}: 3030, 2940, 2870, 1460, 1120, 930, 750. ^1H NMR, δ: 1.08—2.18 (m, 16 H, CH, CH_2); 2.42—2.98 (m, 4 H, CH_2S); 5.67 (m, 4 H, CH=CH). MS, *m/z*: 248 [M$^+$]. Found (%): C, 77.36; H, 9.70; S, 12.94. $C_{16}H_{24}S$. Calculated (%): C, 77.42; H, 9.68; S, 12.90.

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