Polyfunctional Compounds Containing the 4,6-Dialkoxy-7-arylthioheptene Moiety as Synthetically Useful Intermediates. The Course of the Lewis Acid Induced Transformations

Dmitriy S. Chekmarev,* Margarita I. Lazareva, Georgy V. Zatonsky, Andrei V. Maskaev, Ron Caple, William Smit*

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1. **4,6-Dimethoxy-4-methyl-7-(p-tolylthio)hept-1-ene (4a,b).** ^1H NMR (for the mixture **4a,b**) (CDCl_3) δ : 1.13 and 1.16 (2s, 3H, Me), 1.68-1.93 (m, 2H, CCH_2CH), 2.26 (m, 2H, $\text{CH}_2\text{CH=}$), 2.32 (s, 3H, *MeAr*), 2.9-3.14 (m, 2H, CH_2S), 3.20 and 3.31 (2s, 6H, MeO), 3.51 (m, 2H, CHOMe), 5.04 (m, 2H, $\text{CH}_2=$), 5.82 (m, 1H, CH=), 7.08 and 7.26 (dd, 4H_{arom}). ^{13}C -NMR (CDCl_3) δ : 21.0 (*MePh*), 22.9 and 23.2 (*MeCO*) 38.7 and 38.8 (CH_2S), 40.9 and 41.6 (CCH_2CH), 42.9 ($\text{CH}_2\text{CH=}$), 49.0 (*MeOC*), 56.5 and 56.6 (*MeOCH*), 75.6 and 75.7 (COMe), 76.5 and 76.6 (CHOMe), 117.5 and 117.6 ($\text{CH}_2=$), 129.6 (2CH-arom), 129.9 (2CH-arom), 132.7 and 136.0 (2C-arom), 134.0 and 134.5 (CH=)
2. **4,6-Dimethoxy-5,5-dimethyl-7-(p-tolylthio)hept-1-ene (5a,b).** ^1H NMR (for the mixture **5a,b**) (CDCl_3) δ : 0.86 and 0.97 (2s, 6H, Me_2), 2.05-2.25 (m, 2H, $\text{CH}_2\text{C=}$), 2.33 (s, 3H, *MeAr*), 2.95 and 3.20 (2m, 2H, CH_2S), 3.20 - 3.45 (m, 2H, CHOMe), 3.43, 3.45, 3.51, and 3.53 (4s, 3H, MeO), 5.0 - 5.15 (m, 2H, $\text{CH}_2=$), 5.83 - 6.05 (m, 1H, CH=), 7.10 and 7.32 (2d, 4H, H_{ar}). ^{13}C -NMR (CDCl_3) δ : 18.7, 18.8, 19.7 and 19.9 (2Me), 20.9 and 21.0 (*MePh*), 35.1 and 35.4 (CH_2), 36.9 and 37.3 (CH_2S), 43.8 and 44.2 (C), 59.4, 59.8, 60.4 and 61.2 (2MeO), 84.3, 84.9, 85.5 and 85.8 (2CHOMe), 116.0 and 116.0 ($\text{CH}_2=$), 129.6 and 129.8 (2CH-arom), 130.0 and 130.2 (2CH-arom), 133.5, 133.5, 137.1 and 137.3 (2C-arom), 136.0 and 136.1 (CH=);
3. **5-Methoxy-3-methyl-3-(p-tolylthiomethyl)cyclohexene (19a,b) and 3-methoxy-5-methyl-5-(p-tolylthiomethyl)cyclohexene (19c,d)** **19a : 19b : 19c : 19d = 1 : 1 : 1 : 1**). ^1H NMR (CDCl_3) δ : 1.08, 1.14, 1.17 and 1.19 (4s, 3H, Me), 1.35, 1.5, 1.6 and 1.7 (4dd, 2H, CH_2), 1.9-2.35 (m, 2H, $\text{CH}_{2,\text{all}}$), 2.32 (s, 3H, *MeAr*), 2.9-3.1 (4dd, 2H, CH_2S), 3.26, 3.35, 3.39 and 3.40 (4s, 3H, MeO), 3.45-3.6 (2m, 1H, CHOMe), 3.78 and 3.88 (2m, 1H, CHOMe), 5.5, 5.6, 5.75 and 5.80 (4m, 1H, CH=), 7.09 and 7.28 (dd, 4H_{arom}). Ratio of isomers was estimated by the integration of non-overlapping signals. Similarly four sets of closely related signals were observed in ^{13}C NMR. ^{13}C -NMR (CDCl_3) δ : 21.2 (*MePh*), 24.5, 27.7, 28.0 and 28.3 (4Me), 32.0, 37.0, 38.0, 38.9, 39.1, 39.5, 40.1, 45.7, 74.8, 49.1 and 49.2 (11 CH_2), 56.0

and 56.1 (2MeO), 74.6 and 74.1 (2CHOMe), 123.7, 123.9, 127.3, 127.5, 128.1 and 128.1 (6CH=), 129.7 and 129.9 (4CH-arom), 130.5, 130.6, 134.8 and 135.3 (4C-arom).

5. **5-Methoxy-5-methyl-3-(*p*-tolylthiomethyl)cyclohexene (20a,b)** (**20a** : **20b** = 1.5 : 1, GC-MS) ¹H NMR (for **20a,b**) (CDCl₃) δ: 1.15 and 1.20 (2s, 3H, Me), 1.25 (m, 2H), 1.90 - 2.25 (m, 2H, CH_{2,all}), 2.31 (s, 3H, MeAr), 2.90 (m, 2H, CH₂S), 3.15 and 3.25 (2s, 3H, MeO), 5.60 - 5.60 (CH=CH), 7.09 and 7.27 (dd, 4H_{arom}).

6. (*E*)-**6-methoxy-4-methyl-7-(*p*-tolylthio)hepta-1,3-diene (21)** (yield 25%, R_f 0.7, hexane-ether 15 : 1). ¹H NMR (CDCl₃) δ: 1.77 (s, 3H, Me), 2.33 (s, 3H, MeAr), 2.36 (m, 2H_{all}), 3.00 (m, 2H, CH₂S), 3.35 (s, 3H, MeO), 3.48 (m, 1H, CHOMe), 5.06 (m, 2H, CH₂=), 5.88 (dd, 1H, C=CH-CH=, J=10.5), 6.55 (m, 1H, CH=CH₂), 7.10 and 7.27 (dd, 4H_{arom}).

7. *trans*-**2-(*E*-2',5'-Dimethylhexa-3',5'-dien-2'-yl)-3-(*p*-tolylthio)tetrahydropyran (31)**. ¹H NMR (CDCl₃) δ: 1.19 (s, 6H, Me₂), 1.61 and 1.89 (2m, 4H, 2CH₂), 1.89 (s, 3H, MeC=C), 2.34 (s, 3H, Me_{arom}), 3.09 (m, 2H, CHS, CHO), 3.42 and 3.98 (2m, 2H, CH₂O), 4.92 (s, 2H, C=CH₂), 5.93 (d, 1H, C-CH=CH, J=17.0), 6.17 (d, 1H, C-CH=CH, J=17.0), 7.1 and 7.32 (2d, 4H_{arom}). ¹³C NMR (CDCl₃) δ: 18.8 (MeC=), 21.0 (MeAr), 22.7 and 26.4 (2Me), 24.4 and 29.8 (2CH₂), 41.0 (C_{quat}), 46.8 (CHS), 67.2 (CH₂O), 87.4 (CHO), 114.5 (CH₂=), 129.6 (CH=CH), 131.0 and 137.1 (4CH_{arom}), 138.1 (CH=CH), 142.5 (C=).

Figure S1. ¹H NMR spectra of **1-Chloro-3-methoxy-5-(*p*-tolylthiomethyl)cyclohexane (17a 1,5-cis, 1,3-trans)** in CDCl₃

Figure S2. ¹H NMR spectra of **1-Chloro-3-methoxy-5-(*p*-tolylthiomethyl)cyclohexane (17b 1,3,5- cis)** in CDCl₃

Figure S3. ¹H NMR spectra of *cis*-1-Methoxy-1-(*E*-penta-2',4'-dienyl)-2-(*p*-tolylthio)cyclopentane (**29**) in CDCl₃

Smit B

Figure S4. Copy of ^1H NMR spectra of intermediate bicyclic thiophanium salt **25** in CD_2Cl_2 .

Smit B

JAB-6
JAX = 14.3

Figure S5. Copy of partial ^1H NMR spectra (from 1.1 ppm to 3.0 ppm) of intermediate bicyclic thiophanium salt 25 in CD_2Cl_2 .

Smit B

Figure S6. Copy of ^{13}C NMR spectra of intermediate bicyclic thiophanium salt 25 in CD_2Cl_2 .

Smit B JMOD

Current Data Parameters
NAME miaz
EXPNO 22
PROCNO 1

F2 - Acquisition Parameters
Date_ 990410
Time 20.54
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG jmod
TD 32768
SOLVENT D2O
NS 1596
DS 0
SWH 27777.777 Hz
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AQ 0.5898740 sec
RG 2298.8
DM 18.000 usec
DE 6.00 usec
TE 303.0 K
P1 6.30 usec
p2 12.60 usec
d13 0.00000300 sec
CNS111 1.0000000
CNS12 150.0000000
d20 0.00666667 sec
DELTA 0.00000802 sec
PL12 18.00 dB
D1 0.50000000 sec
CPDPRG2 Waltz16
PCPD2 91.00 usec
SF02 500.1314600 MHz
NUC2 1H
PL2 120.00 dB
SF01 125.7697390 MHz
NUC1 13C
PL1 0.00 dB

F2 - Processing parameters
SI 16384
SF 125.7577972 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.00 cm
F1P 150.789 ppm
F1 18962.89 Hz
F2P 11.823 ppm
F2 1486.81 Hz
PPMCM 6.31665 ppm/cm
HZCM 794.36749 Hz/cm

Figure S7. Copy of ^{13}C DEPT spectra of intermediate bicyclic thiophanum salt **25** in CD_2Cl_2 .

Current Data Parameters

NAME	EXPNO	PROCNO	PROCNO
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		PULPROG	cosypr
		TO	1024
		SOLVENT	DMSO
		NS	16
		DS	8
		SWH	3501.401 Hz
		FIDRES	3.419337 Hz
		AD	0.1462772 sec
		RG	160
		DM	142.800 usec
		DE	6.00 usec
		TE	303.0 K
		DO	0.00000300 sec
		DT1	0.00000300 sec
		DT2	0.00000300 sec
		PL1	0.00000300 sec
		PL2	120.00 dB
		PL3	1.00000000 sec
		PL4	500.132506 MHz
		NUC1	1H
		PL1	0.00 dB
		PL2	15.00 usec
		PL3	8.00 usec
		PL4	0.0025564 sec
		INQ	

F1 - Acquisition Parameters

NUC0	TO	SWH
1	512	500.1323 MHz
		6.83775 Hz
		7.000 ppm

F2 - Processing Parameters

SI	ST	SI
1024	1024	500.1300066 MHz
		USINE
		0
		0.00 Hz
		0
		0.50

F1 - Processing Parameters

SI	ST	SI
1024	1024	500.1300066 MHz
		USINE
		0
		0.00 Hz
		0

2D NMR plot parameters

CX2	CX1	F2LO
15.00 cm	15.00 cm	5.775 ppm
		2886.19 Hz
		1.283 ppm
		641.69 Hz
		5.768 ppm
		2884.69 Hz
		1.249 ppm
		624.80 Hz
		0.25946 ppm/cm
		145.76594 Hz/cm
		0.30124 ppm/cm
		150.65987 Hz/cm

Figure S8. Copy of 2D COSY spectra of intermediate bicyclic thiophanium salt 25 in CD₂Cl₂.

Smit B COSY

Current Data Parameters		
NAME	EXPNO	PROCNO
F2 - Acquisition Parameters		
Date_	990410	
Time	22.00	
INSTRUM	spect	
PROBHD	5 mm Multin	
PULPROG	cosypr	
TD	1024	
SOLVENT	D2C12	
NS	16	
DS	8	
SWH	3501.401 Hz	
FIDRES	3.419337 sec	
AQ	3.4192772 sec	
RG	180	
GB	143.00 usec	
TE	303.2 K	
TD0	0.00000300 sec	
d11	0.03000000 sec	
d12	0.00002000 sec	
d13	0.00000300 sec	
PL1	120.00 dB	
D1	1.00000000 sec	
SFO1	500.1322505 MHz	
NUC1	1H	
PL1	0.00 dB	
P0	16.00 usec	
P1	8.00 usec	
IN0	0.00026564 sec	
F1 - Acquisition Parameters		
NO0	1	
TD	512	
SFO1	500.1323 MHz	
FIDRES	6.937775 Hz	
SW	7.000 ppm	
F2 - Processing parameters		
SI	1024	
SP	500.1300064 MHz	
SSB	GSINE	
LB	0	
GB	0	
PC	0.50	
F1 - Processing parameters		
SI	1024	
MC2	OF	
SP	500.1300065 MHz	
SSB	GSINE	
LB	0	
GB	0	
2D NMR plot parameters		
CX2	15.00 cm	
FX1	15.00 cm	
FPL0	3.074 ppm	
FZ0	1337.55 Hz	
FPH1	1.290 ppm	
FPH0	645.10 Hz	
FPL1	5.747 ppm	
FIL0	2074.73 Hz	
FPH1	1889.73 ppm	
FPH0	1.1899 ppm/cm	
FZPCNM	59.4865 Hz/cm	
FPHPCNM	0.43634 ppm/cm	
FZPCNM	85.18679 Hz/cm	

Figure S9. Copy of partial 2D COSY spectra (from 1.3 ppm to 3.0 ppm by 3.8 to 5.7 ppm) of intermediate bicyclic thiophanium salt **25** in CD₂Cl₂.

Smit B H/C

Current Data Parameters
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PROCNO 1

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PULPROG zgpg30
INSTRUM spect
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DS 16
SWH 3501.401 Hz
FIDRES 3.41937 Hz
AQ 0.146772 sec
RG 2048
DE 142.800 usec
TE 303.2 K
DE 6.00 usec
TE 16.00 usec
P1 32.00 usec
P2 0.0000000 sec
P3 0.0000000 sec
P4 0.0000000 sec
P5 0.0000000 sec
P6 0.0000000 sec
P7 0.0000000 sec
P8 0.0000000 sec
P9 0.0000000 sec
P10 0.0000000 sec
P11 0.0000000 sec
P12 0.0000000 sec
P13 0.0000000 sec
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P16 0.0000000 sec
P17 0.0000000 sec
P18 0.0000000 sec
P19 0.0000000 sec
P20 0.0000000 sec
P21 0.0000000 sec
P22 0.0000000 sec
P23 0.0000000 sec
P24 0.0000000 sec
P25 0.0000000 sec
P26 0.0000000 sec
P27 0.0000000 sec
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P29 0.0000000 sec
P30 0.0000000 sec
P31 0.0000000 sec
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P37 0.0000000 sec
P38 0.0000000 sec
P39 0.0000000 sec
P40 0.0000000 sec
P41 0.0000000 sec
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P91 0.0000000 sec
P92 0.0000000 sec
P93 0.0000000 sec
P94 0.0000000 sec
P95 0.0000000 sec
P96 0.0000000 sec
P97 0.0000000 sec
P98 0.0000000 sec
P99 0.0000000 sec
P100 0.0000000 sec

Figure S10. Copy of 2D HETCOR spectra of intermediate bicyclic thiophanium salt 25 in CD₂Cl₂.

Figure S12. Copy of 2D NOESY spectra of intermediate bicyclic thiophanium salt **25** in CD₂Cl₂.

8mwt D
NOESY

Figure S13. Copy of 2D NOESY spectra of intermediate bicyclic thiophanium salt 25 in CD₂Cl₂.