Cross-coupling of organomanganese derivatives of 3-sulfolenes with allyl and propargyl bromides; a simple synthesis of functionalized 1,3-dienes

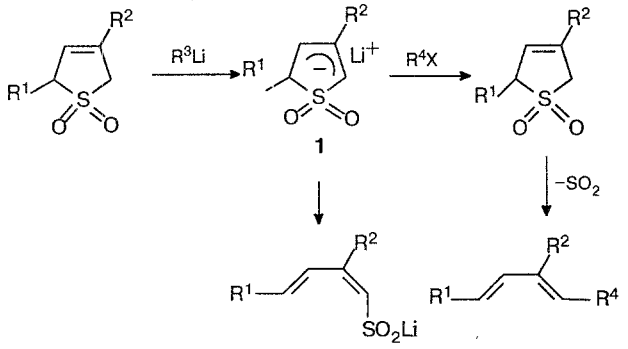
A. N. Kasatkin, Yu. A. Prokopenko, A. M. Khabibov, and G. A. Tolstikov*

Institute of Organic Chemistry, Ural Branch of the Russian Academy of Sciences, 450054 Ufa, Russian Federation.
Fax: +7 (3472) 34 2914

Reactions of organomanganese compounds RMnCl (R = 3-sulfolen-2-yl or 5-methyl-3-sulfolen-2-yl) with allyl or propargyl bromides afford the corresponding 2-substituted or 2,5-disubstituted 3-sulfolenes in high yields. Thermolysis of the cross-coupling products results in 1,3,6-trienes or 1,3-dien-6-ynes.

Key words: (3-sulfolen-2-yl)manganese chloride, (5-methyl-3-sulfolen-2-yl)manganese chloride, allyldemetallation, propargyldemetallation, 2-allyl-substituted 3-sulfolenes, 2-propargyl-substituted 3-sulfolenes, desulfonylation, 1,3,6-trienes, 1,3-dien-6-yne.

The synthesis of substituted 3-sulfolenes is of significant interest due to the possibility of their smooth desulfonylation to the corresponding 1,3-dienes.[1] One of the effective methods of introducing a substituent into the α-position of sulfolenes is the alkylation of the lithium reagents (**1**) obtained *in situ*. As a result of the extremely low thermal stability of carbanions **1**, which are prone to decyclization to salts of dienylsulfonic acids, it is necessary to carry out the reactions at −105 °C [2–4] or to treat the mixture of the starting sulfolene and electrophile with a base (lithium bis(trimethylsilyl)amide).[4–9] Mainly, alkyl and allyl halides without active functional groups were used as substrates.



R^1, R^2 = H, R^1 or R^2 = Alk;

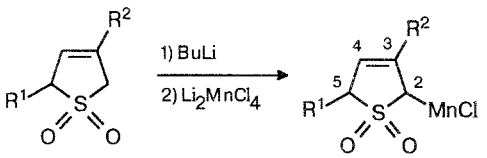
R^3 = Bu, $(Me_3Si)_2N$; R^4 = Me_3Si, Alk, All*, $PhCH_2$;

X = Br, I.

* All = allyl.

We found that the substitution of reagents **1** for the corresponding manganese(II)[10,11] derivatives made it possible to expand the array of allyl-type halides which can be introduced into this reaction.

Organomanganese compounds **2**—**4** were prepared *in situ* by the sequential treatment of 3-sulfolene, 2-methyl-, and 3-methyl-3-sulfolene with butyllithium (THF—HMPA, −105 °C, 10 min) and Li_2MnCl_4 (−105 → −78 °C, 30 min);** in comparison with lithium reagents they are much more stable. Thus, (3-sulfolen-2-yl)lithium totally decomposes even at −78 °C, but hydrolysis of complex **2** during 6 h after its heating to 20 °C gives the starting sulfolene in 70 % yield.



2: $R^1 = R^2 = H$

3: R^1 = Me; R^2 = H

4: R^1 = H, R^2 = Me

The reactions of (3-sulfolen-2-yl)manganese chloride (**2**) with allyl and propenyl bromides were per-

** The location of the MnCl fragment in position 2, not 5 of the sulfolene ring in complexes **3** and **4** is confirmed by the data of regioselectivity of lithiation of 2- and 3-alkyl-3-sulfolenes;[3,8] the corresponding tributylstannyl derivatives possess the analogous structure.[12]

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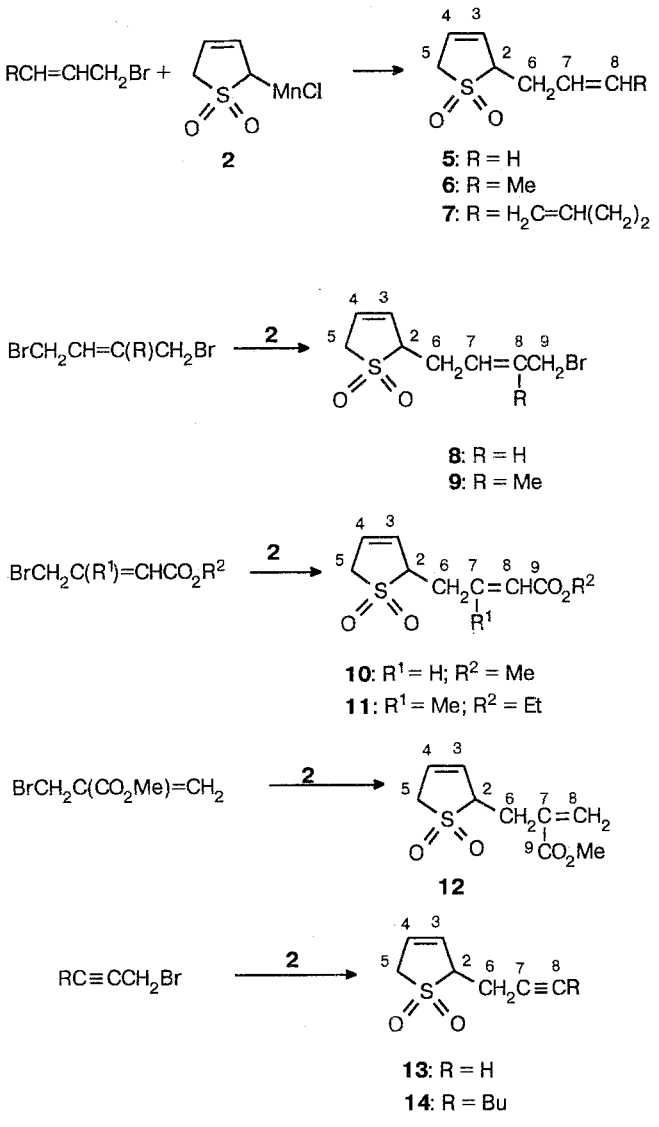
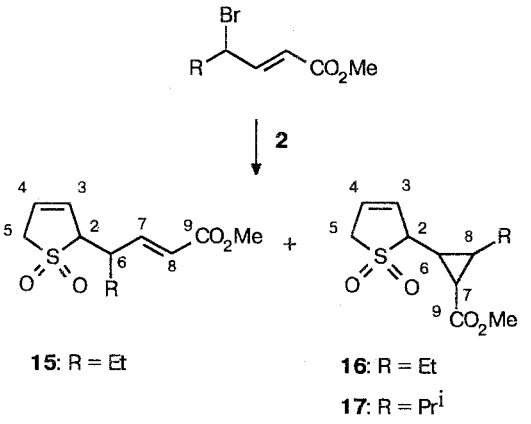
Scheme 1



formed with heating from −78 to 20 °C (3 h) giving 2-substituted 3-sulfolenes (**5**—**14**) in a high yield (Table 1). If crotyl or 2,7-octadienyl bromide are used, the cross-coupling proceeds with the participation of only the primary C-atom of the substrate. 1,4-Dibromo-2-butene and 1,4-dibromo-2-methyl-2-butene give predominantly the products of monosulfolenylation **8** and **9**, respectively. The selective formation of the products of mono-substitution is also observed upon the reaction of allylic 1,4-dibromides with allylmanganese halides.[13] The reactions of complex **2** with the bromo derivatives of methyl crotonate, ethyl 3-methyl-2-butenoate, and methyl methacrylate are characterized by total retention of the alkoxycarbonyl group and they give α,β-unsaturated esters **10**—**12**, containing the sulfolenyl fragment. The reactions of reagent **2** with 2-propynyl and 2-heptynyl bromides afford propargylsulfolenes **13** and

Scheme 2



14, respectively, without any admixture of the corresponding allenes (Scheme 1).

According to the data of ^1H and ^{13}C NMR spectroscopy, crotyl bromide, 2,7-octadienyl bromide, and methyl 4-bromocrotonate give total retention of the geometry of the double bond: product **10** has the *trans*-configuration, and **6** and **7** have the same isomeric composition as the starting allyl bromides (Table 1, entries 2 and 3). In contrast, *trans*-1,4-dibromo-2-butene affords monobromide **8** as a mixture of *cis*- and *trans*-isomers. A change in the geometry of the double bond in favour of the *Z*-isomer is also observed in the cases of 1,4-dibromo-2-methyl-2-butene and ethyl 4-bromo-3-methyl-2-butenoate (Table 1, entries 5 and 7).

The reaction of complex **2** with methyl 4-bromo-2-hexenoate (Scheme 2) affords a mixture (78 : 22; 69 % total yield) of the cross-coupling product **15** and sulfolene **16**; the latter contains the cyclopropane fragment. If methyl 4-bromo-5-methyl-2-hexenoate is used, only cyclopropane **17** is obtained in 23 % yield; this low yield is a result of vigorous polymerization. An apparent route of formation of products **16** and **17** includes the conjugated addition of reagent **2** to α,β-unsaturated substrates followed by cyclization of bromo-containing manganese enolates. The reaction of alkyl 4-bromocrotonates and the derivatives of (2-bromoalkylidene)malonic acids with allylmanganese halides proceeds in the same manner.[14,15] The presence of only one pattern of signals in the ^{13}C NMR spectra of cyclopropanes **16**, **17** attests to the fact that only one of the eight possible diastereomers is obtained.

Reactions of (5-methyl-3-sulfolen-2-yl)manganese chloride (**3**) with allyl and propargyl bromides (Scheme 3) are performed analogously with those of complex **2** and give 2,5-disubstituted 3-sulfolenes (**18**—**22**) (Table 1). A satisfactory yield of alkyne **22** can be achieved using at least 3 eq. of the manganese derivative (introduction of 2 eq. of **3** decreases the yield of product **22** from 64 to 36 %).

Table 1. Reactions of (3-sulfolen-2-yl)- (**2**) and (5-methyl-3-sulfolen-2-yl)manganese chlorides (**3**) with allyl and propargyl bromides

Reagents and conditions: THF—HMPA (10 : 1), −78 → 20 °C, 3 h, $[reagent]_0$: $[substrate]_0$ = 2 : 1; thermolysis of the reaction products: HMPA (A) or EtOH, 2 eq. of K_2CO_3 (B), 125 °C, 2 h

Entry	RMnCl	Bromide (E/Z)[a]	Product of alkylation			Conditions of thermolysis	Product of thermolysis		
			Compound	E/Z[a]	Yield (%)[b]		Compound	E/Z[a,c]	Yield (%)
1	**2**	CH_2=$CHCH_2Br$	**5**		62				
2	**2**	MeCH=$CHCH_2Br$ (86 : 14)	**6**	86 : 14	65				
3	**2**	H_2C=$CH(CH_2)_3CH$=$CHCH_2Br$ (80 : 20)	**7**	81 : 19	70	B	**24**	80 : 20	73
4	**2**	$BrCH_2CH$=$CHCH_2Br$ (100 : 0)	**8**	32 : 68	59	A	**25**	> 95 : 5	60
5	**2**	$BrCH_2CH$=$C(Me)CH_2Br$ (75 : 25)	**9**	60 : 40	54	B	**26**	85 : 15	63
6	**2**	$BrCH_2CH$=$CHCO_2Me$ (100 : 0)	**10**	100 : 0	82	A	**28**	100 : 0	51
7	**2**	$BrCH_2C(Me)$=$CHCO_2Et$ (55 : 45)	**11**	43 : 57	72	A	**29**	44 : 56	47
8	**2**	$BrCH_2C(CO_2Me)$=CH_2	**12**		77	A	**30**		63
9	**2**	HC≡CCH_2Br	**13**		43				
10	**2**	BuC≡CCH_2Br	**14**		67	A	**31**		59
11	**3**	CH_2=$CHCH_2Br$	**18**+**23**[d]		55				
12	**3**	$BrCH_2CH$=$CHCH_2Br$ (100 : 0)	**19**	62 : 38	42	B	**27**	>95 : 5	60
13	**3**	$BrCH_2CH$=$CHCO_2Me$ (100 : 0)	**20**	100 : 0	60				
14	**3**	$BrCH_2C(CO_2Me)$=CH_2	**21**		65				
15[e]	**3**	BuC≡CCH_2Br	**22**		64	B	**32**		64

[a] According to ^1H and ^{13}C NMR spectroscopy data. [b] Yields of the products isolated by column chromatography are presented. [c] **6**E/**6**Z; other double bonds have trans-configuration. [d] **18** (2,5-trans-isomer): **23** (2,5-cis-isomer) = 80 : 20. [e] $[Reagent]_0$: $[substrate]_0$ = 3 : 1.

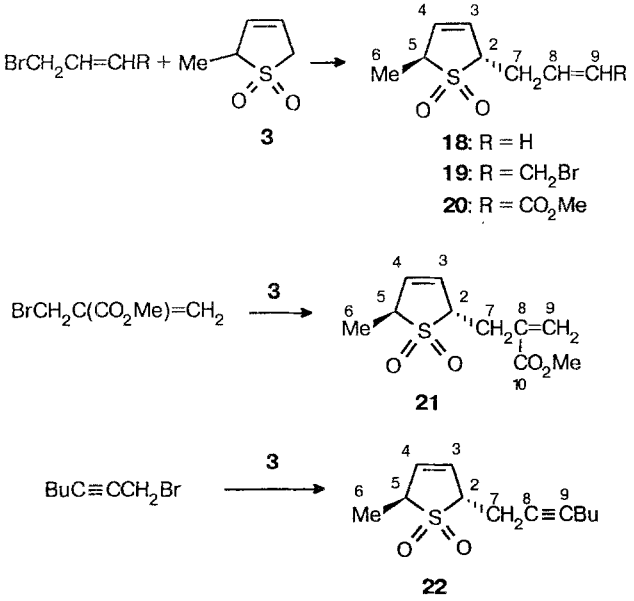
The sulfolenes obtained have the *trans*-2,5-configuration, confirmed by the comparison of the ^{13}C NMR spectra of compounds **18**, **19**, **22** with those of the corresponding *cis*-isomers (the signals of the α-carbon atoms of *cis*-2,5-disubstituted 3-sulfolenes are shifted downfield[16]). Partial isomerization (30—40 %) of products **19**, **22** proceeds easily in the presence of 10 mol. % NaOH in methanol (20 °C, 3 h);[8] isomerization of *trans*-2-allyl-5-methyl-3-sulfolene (**18**) to the *cis*-2,5-derivative (**23**) take place even during its isolation by column choromatography (Table 1, entry 11). In all cases substituted 2-sulfolenes are formed as by-products.

In contrast to complexes **2** and **3**, (3-methyl-3-sulfolen-2-yl)manganese chloride (**4**), in which the reaction center is shielded by a methyl group, does not react with allyl and propargyl bromides under the conditions studied.

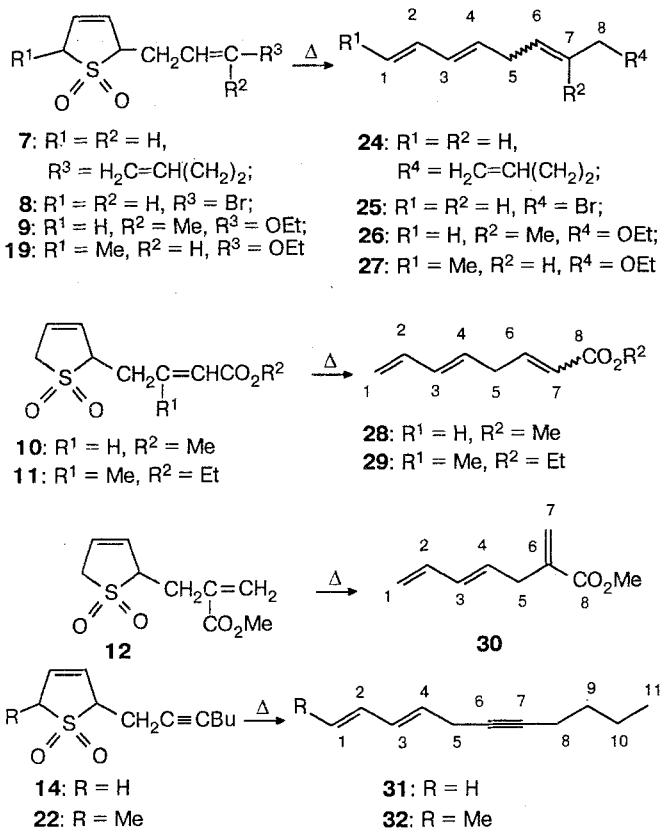
Heating sulfolenes **8**, **10—12**, **14** in HMPA and sulfolenes **7**, **9**, **19**, **22** in ethanol in the presence of K_2CO_3[8,9] (125 °C, 2 h) gives tetraene **24**, trienes **25—30**, and dienynes **31**, **32** (Table 1). Desulfonylation of bromides **9**, **19** is accompanied by replacement of the allyl Br atom by an ethoxy group (Scheme 4).

In all cases the formation of the diene system is characterized by high stereoselectivity: the C(3)=C(4) bonds in products **24—26**, **28—31**; the C(1)=C(2) and C(3)=C(4) bonds in products **27**, **32** have exclusively the *trans*-configuration. During the synthesis of tetraene **24** and unsaturated esters **28**, **29** total retention of the geometry of the C(6)=C(7) bonds is observed (Table 1, entries 3, 6, and 7); on the other hand, thermolysis of the bromo-containing sulfolenes **8**, **9**, **19**, proceeds with the inversion of the latter in favor of the formation of the *E*-isomers (Table1, entries 4, 5, and 12). The configuration of the products of desulfonylation was

Scheme 3



Scheme 4



determined on the basis of the spin coupling constants of the olefinic protons in the ^1H NMR spectra (14—16 Hz for *trans*-isomers), and the chemical shifts of the carbon atoms of the allyl CH_2- and CH_3-groups in the ^{13}C NMR spectra.

Thus, the reaction of organomanganese derivatives of 3-sulfolenes with allyl and propargyl bromides followed by thermolysis is a convenient and stereoselective method for the synthesis of various unsaturated compounds containing the 1,3-diene fragment.

Experimental

Reactions were monitored by TLC on Silufol UV-254 plates sprayed with $KMnO_4$. The ^1H and ^{13}C NMR spectra were recorded with a Bruker AM-300 (300 MHz) instrument in $CDCl_3$ using tetramethylsilane as the internal standard. The mass spectra were obtained with a MKh-1306 mass spectrometer; the temperature of the reservoir was 100 °C and the ionization energies of the electrons were 70 and 12 eV.

The starting 3-sulfolenes were synthesized by the reaction of SO_2 with butadiene, isoprene, and piperylene in an autoclave at 100 °C.[17] 2,7-Octadienylbromide, 2-heptynylbromide, 1,4-dibromo-2-methyl-2-butene were obtained using known procedures. γ-Bromo-containing α,β-unsaturated esters were prepared by bromination of methyl crotonate, ethyl 3-methyl-2-butenoate, methyl 2-hexenoate, and methyl 5-methyl-2-hexenoate with N-bromosuccinimide in the presence of benzoyl peroxide;[18] methyl 2-(bromomethyl)acrylate was obtained in accordance with the procedure from ref. 19. All the reactions were carried out under dry Ar using absolute solvents. THF was distilled over $LiAlH_4$ prior to use.

Table 2. Elemental analysis data of the newly prepared substituted 3-sulfolenes and their desulfonylation products

Compound	Molecular formula	Found / Calculated (%) C	H	S
6	$C_8H_{12}O_2S$	55.34	6.79	18.41
		55.81	6.98	18.60
7	$C_{12}H_{18}O_2S$	63.85	8.10	14.07
		63.72	7.96	14.16
8	$C_8H_{11}BrO_2S$*	38.41	4.27	12.51
		38.25	4.38	12.75
9	$C_9H_{13}BrO_2S$*	40.95	4.79	12.25
		40.75	4.91	12.08
10	$C_9H_{12}O_4S$	50.43	5.47	14.77
		50.00	5.56	14.81
11	$C_{11}H_{16}O_4S$	54.33	6.42	13.55
		54.10	6.56	13.11
12	$C_9H_{12}O_4S$	50.28	5.35	14.75
		50.00	5.56	14.81
13	$C_7H_8O_2S$	53.64	5.15	20.39
		53.85	5.13	20.51
14	$C_{11}H_{16}O_2S$	62.31	7.43	14.85
		62.26	7.55	15.09
18+23	$C_8H_{12}O_2S$	55.48	6.75	18.51
		55.81	6.98	18.60
19	$C_9H_{13}BrO_2S$*	40.91	4.87	12.00
		40.75	4.91	12.08
20	$C_{10}H_{14}O_4S$	52.34	5.95	13.71
		52.17	6.09	13.91
21	$C_{10}H_{14}O_4S$	51.95	6.05	14.05
		52.17	6.09	13.91
22	$C_{12}H_{18}O_2S$	63.98	7.81	14.13
		63.17	7.96	14.16
24	$C_{12}H_{18}$	88.71	11.22	
		88.89	11.11	
25	$C_8H_{11}Br$*	51.47	5.64	
		51.34	5.88	
26	$C_{11}H_{18}O$	79.20	10.77	
		79.52	10.84	
27	$C_{11}H_{18}O$	79.14	10.69	
		72.52	10.84	
28	$C_9H_{12}O_2$	71.37	7.79	
		71.05	7.89	
29	$C_{11}H_{16}O_2$	73.45	8.80	
		73.33	8.89	
30	$C_9H_{12}O_2$	71.27	7.82	
		71.05	7.89	
31	$C_{11}H_{16}$	88.93	10.74	
		89.19	10.81	
32	$C_{12}H_{18}$	88.70	11.25	
		88.89	11.11	

* Br, found/calculated (%): 31.52/31.87 (**8**), 29.78/30.19 (**9**), 30.33/30.19 (**19**), 42.51/42.78 (**25**).

Table 3. The ^1H NMR spectra of the substituted sulfolenes, δ, (J/Hz)

Compound	Protons of sulfolene cycle				Other signals
	H-2	H-5	H-3	H-4	
6	3.5—3.8 m		6.05 m		1.7 (d, J = 5, 3 H, CH_3), 2.1—2.8 (m, 2 H, CH_2), 5.4—5.8 (m, 2 H, CH=)
7	3.5—3.7 m		5.95 m		1.4 (t.t, $J_1 = J_2$ = 7.3, 2 H, CH_2), 1.9—2.07 (m, 4 H, CH_2C=), 2.25 (d.d.d, J_1 = 14.6, J_2 = 7.7, J_3 = 7.3, 1 H, CH_2C=), 2.57 (d.d.d, J_1 = 14.6, J_2 = 7.6, J_3 = 6.3, 1 H, CH_2C=), 4.73—4.97 (m, J_1 = 15.3, J_2 = 7.7, 2 H, CH_2=), 5.4 (d.t, 1 H, CH=,), 5.55 (d.t, J_1 = 15.3, J_2 = 7.1, 1 H, CH=), 5.6—5.8 (m, 1 H, C<u>H</u>=CH_2) (*E*-isomer)
8	3.75 m		6.07 m		2.47—2.85 (m, 2 H, CH_2), 3.95 и 4.06 (d, J = 6, 2 H, CH_2Br), 5.65—5.9 (m, 2 H, CH=)
9	3.6—3.8 m		5.9—6.1 m		1.72 и 1.75 (s, 3 H, CH_3), 2.35—2.5 (m, 1 H, CH_2), 2.55—2.7 (m, 1 H, CH_2), 3.92 и 3.98 (s, 2 H, CH_2Br), 5.55 и 5.62 (t, J = 7.2, 1 H, CH=)
10	3.6—4.0 m		6.1 m		2.3—3.1 (m, 2 H, CH_2), 3.75 (s, 3 H, CH_3O), 5.9 (d, J = 15, 1 H, $CHCO_2$), 7.0 (d.t, J_1 = 15, J_2 = 7, 1 H, CH=)
***E*-11**	3.81 m	3.7 m	5.98 m		1.28 (t, J = 7.8, 3 H, CH_3), 2.15 (s, 3 H, CH_3C=), 2.3 (d.d, J_1 = 12, J_2 = 7.7, 1 H, CH_2),3.15 (d.d, J_1 = 13.2, J_2 = 7.2, 1 H, CH_2), 4.05 (q, J = 7.8, 2 H, CH_2O), 5.77 (s, 1 H, CH=)
***Z*-11**	3.89 t (7.5)	3.7 m	5.98 m		1.22 (t, J = 7.8, 3 H, CH_3), 2.15 (s, 3 H, CH_3C=), 2.3 (d.d, J_1 = 14.7, J_2 = 9.2, 1 H, CH_2), 2.76 (d.d, J_1 = 14.7, J_2 = 6.1, 1 H, CH_2), 4.07 (q, J = 7.8, 2 H, CH_2O), 5.71 (s, 1 H, CH=)
12	3.98 m	3.75 m	5.98—6.15 m		2.62 (d.d, J_1 = 14.6, J_2 = 7.5, 1 H, CH), 2.98 (d.d, J_1 = 14.6, J_2 = 7.3, 1 H, CH_2), 3.79 (s, 3 H, CH_3O), 5.83 (s, 1 H, CH_2=), 6.35 (s, 1 H, CH_2=)
13	3.78 m		6.15 m		2.12 (t, J = 2, 1 H, CH≡), 2.58 (d.d.d, J_1 = 16.6, J_2 = 8.2, J_3 = 2.0, 1 H, CH_2) 2.82 (d.d.d, J_1 = 16.6, J_2 = 5.9, J_3 = 2.0, 1 H, CH_2)
14	3.5—3.9 m		6.14 m		0.9 (t, J = 8, 3 H, CH_3), 1.1—1.6 (m, 4 H, CH_2), 1.9—2.3 (m, 2 H, CH_2C≡), 2.32—3.0 (m, 2 H, CH_2C≡)
15[a]	3.7 m		6.0 m		0.75 (t, J = 7.2, 3 H, CH_3), 1.3—1.6 (m, 2 H, CH_2), 2.67 (m, 1 H, CHC=), 3.65 (s, 3 H, CH_3O), 5.92 (d, J = 15.6, 1 H, CH=), 6.63 (d.d, J_1 = 15.6, J = 10.0, 1 H, CH=)
16[a]	3.26 d (9.2)	3.7 m	6.0 m		0.85 (t, J = 7.2, 3 H, CH_3), 1.3—1.9 (m, 5 H, CH_2+CH), 3.65 (s, 3 H, CH_3O)
17	3.46 d (10.3)	3.6—3.8 m	5.9—6.1 m		1.07 и 1.16 (d, 6 H, CH_3, J = 6.3), 1.2—1.9 (m, 4 H, CH), 3.65 (s, 3 H, CH_3O)
18[b]	3.6—3.8 m		5.05—5.25 m		1.39 (d, J = 7.2, 3 H, CH_3), 2.34 (d.d.d, J_1 = 14.8, $J_2 = J_3$ = 7.7, 1 H, CH_2), 2.71 (d.d.d, J_1 = 14.8, $J_2 = J_3$ = 6.3, 1 H, CH_2), 5.7—6.0 (m, 3 H, CH=)
19	3.6—3.8 m		5.9—6.05 m		1.43 (d, J = 7.5, 3 H, CH_3), 2.4 (d.d.d, J_1 = 14.7, $J_2 = J_3$ = 7.0, 1 H, CH_2), 2.71 (d.d.d, J_1 = 14.7, $J_2 = J_3$ = 6.2, 1 H, CH_2), 3.92 (d, J = 6.4, 2 H, CH_2Br), 5.7—5.9 (m, 2 H, CH=) (*E*-isomer); 4.03 (d, J = 5.3, 2 H, CH_2Br) (*Z*-isomer)
20	3.55—3.95 m		6.0 m		1.4 (d, J = 6.2, 3 H, CH_3), 2.3—3.0 (m, 2 H, CH_2), 3.7 (s, 3 H, CH_3O), 5.9 (d, J = 15.0, 1 H, $CHCO_2$), 7.0 (d.t, J_1 = 15, J_2 = 7, 1 H, CH=)
21	3.83m	3.55—3.75 m	5.88 m		1.32 (d, J = 7.2, 3 H, CH_3), 2.51 (d.d, J_1 = 14.6, J_2 = 7.5, 1 H, CH_2), 2.9 (d.d, 1 H, J_1 = 14.6, J_2 = 7.2, CH_2), 3.68 (s, 3 H, CH_3O), 5.74, 6.25 (s, 2 H, CH_2=)
22	3.65—3.85 m		6.04 m		0.9 (t, J = 8, 3 H, CH_3), 1.2—1.6 (m, 4 H, CH_2), 1.4 (d, J = 7.6, 3 H, CH_3), 2.13 (m, 2 H, CH_2C≡), 2.35—2.85 (m, 2 H, CH_2C≡)

[a,b] The compounds were identified in a mixture.

Table 4. The ^{13}C NMR spectra of substituted 3-sulfolenes, (δ)

Compound	C-2	C-3	C-4	C-5	Other signals
5	63.7 d	129.8 d	123.4 d	55.8 t	32.6 (t, C-6), 132.8 (d, C-7), 118.5 (t, C-8)
6	64.3 d	130.0 d	123.2 d	55.8 t	31.6 (t, C-6), 125.3 (d, C-7), 129.4 (d, C-8), 17.8 (q, CH_3) (*E*-isomer); 26.2 (t, C-6), 124.4 (d, C-7), 127.9 (d, C-8), 12.9 (q, CH_3) (*Z*-isomer)
***E*-7**	64.01 d	129.73 d	122.98 d	55.55 t	32.34 (t, C-6), 124.18 (d, C-7), 134.40 (d, C-8), 28.12 (t, CH_2), 31.37, 31.58 (t, CH_2C=), 114.37 (t, CH_2=), 138.30 (d, CH=)
***Z*-7**	64.01 d	129.73 d	123.11 d	55.51 t	26.49 (t, C-6), 123.40 (d, C-7), 133.81 (d, C-8), 26.24, 33.11 (t, CH_2C=), 28.20 (t, CH_2), 114.47 (t, CH_2=), 138.22 (d, CH=)
8	63.51 d	129.38 d	123.63 d	55.62 t	31.01 (t, C-6), 129.56, 130.35 (d, C-7, C-8), 44.32 (t, C-9) (*E*-isomer); 31.01 (t, C-6), 129.25, 130.16 (d, C-7, C-8), 44.32 (t, C-9) (*Z*-isomer)
***E*-9**	63.64 d	129.35 d	123.56 d	55.55 t	27.33 (t, C-6), 124.01 (d, C-7), 135.65 (s, C-8), 51.38 (t, C-9), 14.43 (q, CH_3) (*E*-isomer)
***Z*-9**	63.58 d	129.41 d	123.56 d	55.55 t	27.11 (t, C-6), 124.47 (d, C-7), 135.97 (s, C-8), 40.30 (t, C-9), 14.95 (q, CH_3) (*Z*-isomer)
10	67.2 d	129.4 d	124.5 d or 124.1 d	55.6 t	124.1 or 124.5 (d, C-4, C-8), 31.1 (t, C-6), 142.4 (d, C-7), 166.2 (s, C-9), 51.6 (q, CH_3O)
***E*-11**	61.58 d	130.05 d	123.69 d	55.48 t	38.92 (t, C-6), 152.98 (s, C-7), 118.69 (d, C-8), 165.82 (s, C-9), 59.66 (t, CH_2O), 14.07, 18.52 (q, CH_3)
***Z*-11**	63.24 d	129.38 d	122.97 d	55.32 t	31.61 (t, C-6), 154.28 (s, C-7), 119.09 (d, C-8), 165.69 (s, C-9), 59.71 (t, CH_2O), 14.07, 25.55 (q, CH_3) (*Z*-isomer)
12	62.59 d	129.40 d	123.57 d	55.96 t	31.14 (t, C-6), 135.49 (s, C-7), 128.97 (t, C-8), 166.66 (s, C-9), 52.13 (q, CH_3O)
13	62.7 d	128.9 d	124.3	55.3 t	18.8 (t, C-6), 78.5 (s, C-7), 71.5 (s, C-8)
14	62.8 d	128.9 d	123.7 d	55.4 t	18.7 (t, C-6), 74.0 (s, C-7), 82.9 (s, C-8), 13.1 (q, CH_3), 17.9 (t, $CH_2C\equiv$), 21.4, 30.4 (t, CH_2)
15[a]	66.88 d	127.94 d	124.47 d	55.99 t	124.47 (d, C-8), 43.56 (d, C-6), 146.05 (d, C-7), 166.21 (s, C-9), 11.36 (q, CH_3), 25.48 (t, CH_2), 51.59 (q, CH_3O)
16[a]	67.37 d	128.52 d	124.19 d	55.40 t	22.27, 24.39, 29.01 (d, C-6, C-7, C-8), 171.44 (s, C-9), 13.24 (q, CH_3), 19.77 (t, CH_2), 51.80 (q, CH_3O)
17	63.33 d	129.95 d	123.80 d	56.16 t	23.95, 25.68, 27.80 (d, C-6, C-7, C-8), 172.93 (s, C-9), 21.61, 22.74 (q, CH_3), 35.80 (d, CH), 51.92 (q, CH_3O)
18[b]	62.80 d	127.82 d	130.33 d	59.54 d	32.68 (t, C-7), 132.70 (d, C-8), 118.66 (t, C-9)
23[b]	63.64 d	127.65 d	130.02 d	60.09 d	13.12 (q, C-6), 32.85 (t, C-7), 132.70 (d, C-8), 118.66 (t, C-9)
***E*-19**	62.52 d	127.27 d	130.50 d	59.35 d	12.99 (q, C-6), 32.04 (t, C-7), 129.63, 130.16 (d, C-8, C-9), 44.26 (t, CH_2Br)
***Z*-19**	62.52 d	127.32 d	130.50 d	59.35 d	12.99 (q, C-6), 30.85 (t, C-7), 129.41, 129.75 (d, C-8, C-9), 44.26 (t, CH_2Br) (*Z*-isomer)
20	62.0 d	127.1 d	131.1 d	59.5 d	13.1 (q, C-6), 31.2 (t, C-7), 142.5 (d, C-8), 124.4 (d, C-9), 51.6 (q, CH_3O), 166.1 (s, CO_2)
21	61.79 d	127.68 d	130.42 d	59.74 d	13.35 (q, C-6), 31.11 (t, C-7), 135.47 (s, C-8), 128.92 (t, C-9), 166.61 (s, C-10), 51.98 (q, CH_3O)
22	62.73 d	127.81 d	131.00 d	59.79 d	13.50 (q, C-6), 19.39 (t, C-7), 74.35 (s, C-8), 83.55 (s, C-9), 13.08 (q, CH_3), 18.40 (t, $CH_2C\equiv$), 21.90, 30.94 (t, CH_2)

[a,b] The compounds were identified in a mixture.

Reactions of organomanganese derivatives of 3-sulfolenes with allyl and propargyl bromides

A 2.5 *M* solution of BuLi (2 mL, 5 mmol) in hexane was added at −105 °C to a solution of 3-sulfolene (0.6 g, 5.08 mmol) in a mixture of THF (20 mL) and HMPA (2 mL). Then the mixture was stirred for 15 min at −105 °C. A 1.5 *M* solution of Li_2MnCl_4 in THF[10] (11 mL, 5.5 mmol) cooled to −78 °C was added to the resuling solution of (3-sulfolen-2-yl)lithium. The mixture was stirred for 30 min as the temperature rose from −105 to −78 °C, then methyl-4-bromocrotonate (0.447 g, 2.5 mmol) was added. The reaction mixture was heated to 20 °C for 3 h, hydrolyzed with 2 *N* HCl (5 mL), and extracted with ethyl acetate (3 × 6 mL). The organic layer was washed with water (3 × 10 mL), dried over $MgSO_4$, and concentrated. *E*-Methyl-4-(3-sulfolen-2-yl)-2-butenoate (**10**) (0.443 g, 82 % yield) was obtained as a colorless oil using column chromatography (silica gel L 40/100, hexane—EtOAc, 2 : 1).

An analogous procedure was applied to carry out the reactions of (3-sulfolen-2-yl)MnCl (**2**) and (5-methyl-3-sulfolen-2-yl)MnCl (**3**) with allyl, crotyl-, 2,7-octadienyl-, propargyl- and 2-heptynyl bromides; *trans*-1,4-dibromo-2-butene, 1,4-dibromo-2-methyl-2-butene; esters of bromo derivatives of crotonic, dimethylacrylic, methacrylic, *trans*-2-hexenoic and *trans*-5-methyl-2-hexenoic acids (Table 1).

The following products were obtained: 2-allyl-3-sulfolene (**5**)[20], 2-(2-butenyl)-3-sulfolene (**6**), 2-(2,7-octadienyl)-3-sulfolene (**7**), 2-(4-bromo-2-butenyl)-3-sulfolene (**8**), 2-(4-bromo-3-methyl-2-butenyl)-3-sulfolene (**9**), ethyl 3-methyl-4-(3-sulfolen-2-yl)-2-butenoate (**11**), methyl 2-methylene-3-(3-sulfolen-2-yl)propionate (**12**), 2-propargyl-3-sulfolene (**13**), 2-(2-heptynyl)-3-sulfolene (**14**), 2-allyl-5-methyl-3-sulfolene (**18**+ **23**), 2,5-*trans*-2-(4-bromo-2-butenyl)-5-methyl-3-sulfolene (**19**), methyl *E*-4-(*trans*-5-methyl-3-sulfolen-2-yl)-2-butenoate (**20**), methyl 2-methylene-3-(*trans*-5-methyl-3-sulfolen-2-yl)-propionate (**21**), *trans*-2-(2-heptynyl)-5-methyl-3-sulfolene (**22**).

The data of elemental analysis and the ^1H and ^{13}C NMR spectra of the substituted 3-sulfolenes obtained are presented in Tables 2—4.

Thermolysis of 2-allyl- and 2-propargyl-substituted 3-sulfolenes

A. A solution of methyl 4-(3-sulfolen-2-yl)-2*E*-butenoate (**10**) (0.18 g, 0.83 mmol) in 0.5 mL of HMPA was stirred at

Table 5. The ^1H NMR spectra of the products of desulfonylation of substituted 3-sulfolenes, (δ, J/Hz)

Compound	Signals					Other signals
	H-1	H-2	H-3	H-4	5-CH_2	
24	5.12 d (17.0)	6.33 d.d (17.0, 10.4)	6.07 d.d (15.2, 10.4)	5.71 d.t (15.2, 6.5)	2.78 m	1.48 (t.t, $J_1 = J_2 = 7.6$, 2 H, CH_2), 2.0—2.15 (m, 4 H, CH_2C=), 4.9—5.05 (m, 3 H, CH_2=), 5.43 (m, 2 H, CH=), 5.71 (d.t, 1 H, $J_1 = 15.2$, $J_2 = 6.5$, CH_2=CHC<u>H</u>=C<u>H</u>$_2$), 5.75—5.9 (m, $J_1 = 15.2$, $J_2 = 10.4$, 1 H, C<u>H</u>=CH_2) (6*E*-isomer)
25	5.06 d (16.8)	6.25 d.d.d (16.8, 10.4, 10.1)	6.02 d.d (15.1, 10.4)	5.65 m	2.77 d.d (6.4, 6.4)	3.97 (d, $J = 6.8$, 2 H, CH_2Br), 4.95 (d, $J = 10.1$, 1 H, CH_2=)
26	5.03 d (17.0)	6.22 d.d.d (17.0, 10.1)	5.98 d.d (15.1, 10.1)	5.60 d.t (15.1, 6.7)	2.76 d.d (6.7, 6.7)	1.13 (t, $J = 7.0$, 3 H, CH_3), 1.6 (s, 3 H, CH_3C=), 3.37 (q, J=7.0, 2 H, CH_2O), 3.78 (s, 2 H, CH_2O), 4.9 (d, $J = 10.1$, 1 H, CH_2=), 5.38 (t, $J = 6.7$, 1 H, CH=), 1.7 (s, 3 H, CH_3C=), 3.89 (s, 2 H, CH_2O) (6*Z*-isomer)
27	5.65 m	6.03 m	5.65 m	2.82 d.d (6.4 6.4)		1.22 (t, $J = 7.3$, 3 H, CH_3), 1.74 (d, $J = 6.3$, 3 H, CH_3C=), 3.48 (q, $J = 7.3$, 2 H, CH_2O), 3.94 (d, $J = 6.5$, 2 H, CH_2O)
28	5.15 d (16.6)	6.32 d.d.d (16.6, 10.4, 9.9)	6.10 d.d (15.2, 10.4)	5.68 d.t (15.2, 6.7)	2.98 d.t (6.7, 6.7)	3.72 (s, 3 H, CH_3O), 5.02 (d, $J = 9.9$, 1 H, CH_2=), 5.83 (d, $J = 15.6$, 1 H, =$CHCO_2$), 6.98 (d.t, $J_1 = 15.6$, $J_2 = 6.7$, 1 H, C<u>H</u>=$CHCO_2$)
29	5.17 d (16.6)	6.32 m (15.1, 10.4)	6.12 d.d (7.1) 9.6)	5.67 m	2.90 d	1.28 (t, $J = 7.1$, 3 H, CH_3), 2.18 (s, 3 H, CH_3C=), 4.15 (q, J = 7.1, 2 H, CH_2O), 5.05 (d, $J = 10.1$, 1 H, CH_2=) (2*E*-isomer); 1.88 (s, 3 H, CH_3C=), 3.42 (d, J= 7.1, 2 H, CH_2), 5.0 and 5.12 (d, $J = 10.1$ and 16.6, 2 H, CH_2=)
30	5.15 d (16.2)	6.35 d.d.d (16.2, 10.1, 10.1)	6.11 d.d (15.1, 10.1)	5.70 d.t (15.1, 6.9)	3.10 d (6.9)	3.78 (s, 3 H, CH_3O), 5.0 (d, $J = 10.1$, 1 H, C<u>H</u>$_2$=CH), 5.58 and 6.2 (s, 2 H, CH_2=)
31	5.12 d (16.0)	6.1—6.5 m	5.65 d.t (15.8, 6.7)	2.98 m		0.91 (t, $J = 8.0$, 3 H, CH_3), 1.3—1.65 (m, 4 H, CH_2), 2.0—2.3 (m, 2 H, CH_2C≡), 5.05 (d, $J = 9.7$, 1 H, CH_2=)
32	5.65 d.q (14.5, 6.6)	6.05 d.d (14.5, 10.4)	6.25 d.d (15.1, 10.4)	5.55 d.t (15.1, 5.7)	2.98 m	0.93 (t, $J = 7.4$, 3 H, CH_3), 1.2—1.6 (m, 4 H, CH_2), 1.75 (d, $J = 6.6$, 3 H, CH_3C=), 2.1—2.25 (m, 2 H, CH_2C≡)

Table 6. The ^{13}C NMR spectra of the products of desulfonylation of substituted 3-sulfolenes (δ)

Compound	Signals					Other signals
	C-1	C-2	C-3	C-4	C-5	
6*E*-24	115.11 t	137.23 d	133.51 d	127.94 d	35.56 t	131.46, 131.52 (d, C-6, C-7), 33.29 (t, C-8), 28.77 (t, CH_2), 32.04 (t, CH_2C=), 114.51 (t, CH_2=), 138.83 (d, CH=)
6*Z*-24	115.11 t	137.23 d	133.22 d	127.01 d	30.40 t	130.84, 131.26 (d, C-6, C-7), 26.68 (t, C-8), 28.92 (t, CH_2), 33.36 (t, CH_2C=), 114.59 (t, CH_2=), 138.77 (d, CH=) (6*Z*-isomer)
25	115.92 t	136.84 d	133.28 d	127.17 d	34.90 t	131.48, 132.44 (d, C-6, C-7), 45.11 (t, C-8)
6*E*-26	115.10 t	137.14 d	132.88 d	131.23 d	30.80 t	124.47 (d, C-6), 132.88 (s, C-7), 76.44 (t, C-8), 13.82, 15.22 (q, CH_3), 65.17 (t, CH_2O)
6*Z*-26	115.38 t	137.14 d	133.13 d	131.23 d	29.73 t	125.88 (d, C-6, 133.85 (s, C-7), 68.84 (t, C-8), 13.82, 21.64 (q, CH_3), 65.17 (t, CH_2O)
27	127.63 d	131.47 d	132.01 d	129.00 d	35.25 t	131.47 (d, C-6, C-7), 71.24 (t, C-8), 15.27, 18.03 (q, CH_3), 65.55 (t, CH_2O)
28	116.5 t	136.4 d	133.4 d	129.3 d	34.8 t	146.7 (d, C-6), 121.6 (d, C-7), 166.9 (s, C-8), 51.5 (q, CH_3O)
2*E*-29	115.43 t[a]	135.86 d	131.80 d	129.77 d[6]	42.56 t	156.21 (s, C-6), 115.43 (d, C-7), 165.68 (s, C-8), 13.26, 17.90 (q, CH_3), 58.55 (t, CH_2O)
2*Z*-29	114.69 t[a]	135.52 d	132.90 d	128.82 d[6]	35.51 t	156.74 (s, C-6), 115.59 (d, C-7), 165.19 (s, C-8), 13.26, 23.63 (q, CH_3), 58.55 (t, CH_2O)
30	116.07 t	136.80 d	133.14 d	130.91 d	34.75 t	138.99 (s, C-6), 125.67 (t, C-7), 167.39 (s, C-8), 51.96 (q, CH_3O)
31	116.03 t	131.81 d	129.29 d	125.78 d	21.37 t	77.24, 82.61 (s, C-6, C-7), 18.50 (t, C-8), 31.16 (t, C-9), 21.37 (t, C-10), 13.61 (q, C-11)
32	126.06 t	131.12 d	131.40 d	128.22 d	18.60 t	77.53, 82.41 (s, C-6, C-7), 18.03 (t, C-8), 31.29 (t, C-9), 22.05 (t, C-10), 13.65 (q, C-11), 22.05 (q, CH_3C=)

[a,b] An alternate assignment of signals of isomers is possible.

125 °C for 1.5 h while a slight flow of Ar was bubbled through the reaction mixture. After cooling to 20 °C a mixture of pentane (2 mL) and water (2 mL) was added; the aqueous layer was extracted with pentane (2 × 1.5 mL). The organic layer was washed with water (2 × 1.5 mL), dried over $MgSO_4$, and concentrated. Methyl 2*E*,5*E*,7-octatrienoate (**28**) (0.065 g, 51 % yield) was isolated.

Thermolysis of sulfolenes **8**, **11**, **12**, and **14** was performed using analogous procedure (Table 1); 8-bromo-1,3*E*,6*E*-octatriene (**25**), ethyl 3-methyl-2*E*,5,7-octatrienoate (**29**), methyl 2-methylene-4*E*,6-heptadienoate (**30**) and 1,3*E*-undecadien-6-yne (**31**) were obtained.

B. A solution of 2-(2,7-octadienyl)-3-sulfolene (**7**) (0.2 g, 0.88 mmol) in 2 mL of 95% aqueous ethanol and anhydrous K_2CO_3 (0.243 g, 1.76 mmol) was heated in a sealed glass tube at 125 °C for 2.5 h. After cooling to 20 °C pentane (2 mL) and water (5 mL) were added; the aqueous layer was extracted with pentane (2 × 1.5 mL). The organic layer was dried over $MgSO_4$ and concentrated. 1,3*E*,6,11-Dodecatetraene (**24**) (0.104 g, 73 %) was isolated as a mixture of 6*E*- and 6*Z*-isomers (80:20).

Thermolysis of sulfolenes **9**, **19**, and **22** was performed using analogous procedures (Table 1); and 8-ethoxy-7-methyl-1,3*E*,6-octatriene (**26**), 2*E*,4*E*,7*E*-nonatriene (**27**) and 2*E*,4*E*-dodecadien-7-yne (**32**) were obtained.

The elemental analysis data and the ^1H and ^{13}C NMR spectra of the products of desulfonylation are presented in Tables 2, 5 and 6. Peaks of molecular ions are present in the mass spectra of all of the compounds.

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