A Useful Route for Olefin Synthesis: Thermolysis of the Michael Adducts of Aryl Vinyl Sulfoxides

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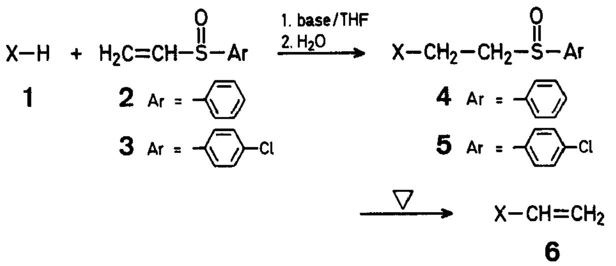
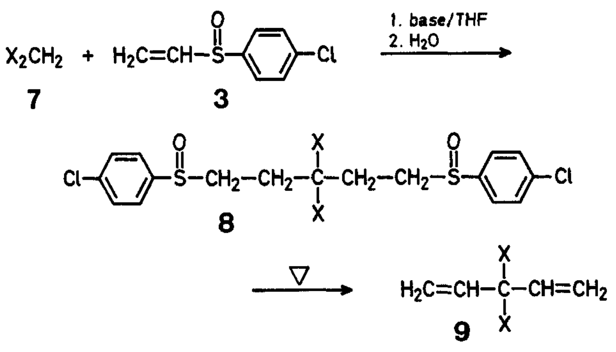
Vinyl sulfoxides react with certain nucleophiles to give Michael-type adducts[1], and sulfoxides are thermally decomposed to give olefins[2]. This report describes an application of these reactions to the introduction of the vinyl group into anionoid reagents (see also Ref.[4]); the reaction of the anionoid reagents **1** with aryl vinyl sulfoxides (**2**, **3**) followed by thermolysis of the resultant alkyl aryl sulfoxides[3,4] (**4**, **5**) proceeds as follows:



The adducts **4f** and **5f** resulting from benzyl alcohol were thermally stable, **5g** from piperidine was thermally decomposed giving diaryl disulfide, but no olefin was isolated. Better results were obtained when 4-chlorophenyl vinyl sulfoxide was employed.

The active methylene compounds **7** were treated with two equivalents of 4-chlorophenyl vinyl sulfoxide (**3**) to give the substituted 1,5-bis[4-chlorophenylsulfinyl]pentanes **8**. Thermolysis of compounds **8** afforded 1,4-pentadienes (**9**) in satisfactory yields.



These reactions require only a catalytic amount of base.

The reaction of aryl 1-bromovinyl sulfoxides with active methylene compounds yields cyclopropylsulfinyl compounds[10]. However, when 1-bromovinyl 4-chlorophenyl sulfoxide (**10**) was treated with 2-nitropropane (**1a**) in a similar manner, the resultant Michael-type adduct was spontaneously dehydrobrominated to give 4-chlorophenyl 3-methyl-3-nitro-1-butenyl sulfoxide (**11**). Heating of **11** with sodium ethoxide in boiling ethanol gave the ethoxylation product **12**, thermolysis of which under reduced pressure led to 2-ethoxy-3-methyl-3-nitro-1-butene (**13**).

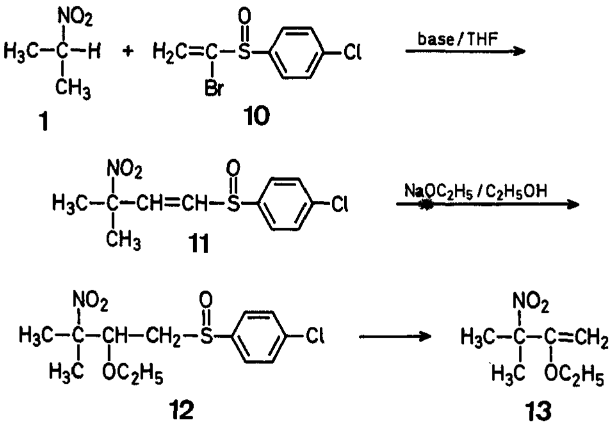
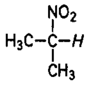
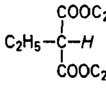
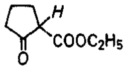
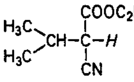
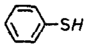
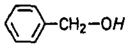
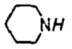
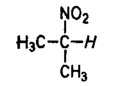
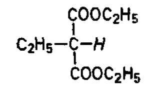
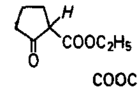
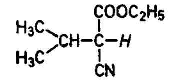
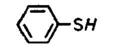


Table 1. Preparation of the Substituted Alkyl Aryl Sulfoxides **4** and **5**

1		4			5		
		Yield [%]	m.p.	Molecular Formula[a]	Yield [%]	m.p.	Molecular Formula[a]
a		87	110–115°	$C_{11}H_{15}NO_3S$ (241.3)	85	123–125°	$C_{11}H_{14}ClNO_3S$ (275.7)
b		95	oil	$C_{17}H_{24}O_5S$ (340.4)	93	oil	$C_{17}H_{23}ClO_5S$ (374.8)
c					67	oil	$C_{16}H_{19}ClO_4S$ (342.8)
d					80	oil	$C_{16}H_{20}ClNO_3S$ (341.8)
e		93	oil	$C_{14}H_{14}OS_2$ (262.3)	86	95–97°	$C_{14}H_{13}ClOS_2$ (296.7)
f		96	oil	$C_{15}H_{16}O_2S$ (260.3)	99	oil	$C_{15}H_{15}ClO_2S$ (294.7)
g					91	oil	$C_{13}H_{18}ClNOS$ (271.7)

[a] The microanalyses showed the following maximum deviation from the calculated values: C, ±0.29; H, ±0.19; Cl, ±0.16; N, +0.13; S, +0.20.

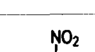
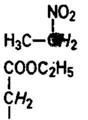
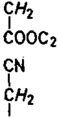
Table 2. Preparation of Alkenes (6) from the Substituted Alkyl Aryl Sulfoxides 4 and 5

		Yield [%]			
	Educt **1**	from **4**	from **5**	b.p./torr	Lit. b.p./torr
a	 $H_3C-C(NO_2)(CH_3)-H$	68	75	151°/760	48–49°/18[5]
b	 $C_2H_5-C(COOC_2H_5)_2-H$	69	86	106°/15	117.5–118°/22[6]
c			75	103°/14	125–126°/20[7]
d	 $(H_3C)_2CH-C(COOC_2H_5)(CN)-H$		80	115°/14	[a]
e		56	81	73°/19	66–68°/5.9[8]

[a] $C_{10}H_{15}NO_2$ (181.2)

		C	H	N
$C_{10}H_{15}NO_2$	calc.	C 66.29	H 8.34	N 7.73
(181.2)	found	66.34	8.30	7.90

Table 3. Preparation of Substituted 1,5-Bis[4-chlorophenylsulfinyl]pentanes (8) and 1,4-Pentadienes (9) from Active Methylene Compounds (7)

		Sulfoxide **8**			Diene **9**	
	Educt **7**	Yield [%]	m.p.	Molecular formula[a]	Yield **8**→**9** [%]	b.p./torr
a	 $H_3C-CH_2(NO_2)$	84	129–131°	$C_{18}H_{19}Cl_2NO_4S_2$ (416.3)	56	[b]
b	 $COOC_2H_5-CH_2-COOC_2H_5$	97	oil	$C_{23}H_{26}Cl_2O_6S_2$ (513.4)	63	118°/14[c]
c	 $CN-CH_2-CN$	98	185°	$C_{19}H_{16}Cl_2N_2O_2S_2$ (439.3)	64	110°/115[d]

[a] The microanalyses showed the following maximum deviation from the calculated values: C, ±0.28; H, ±0.16; Cl, ±0.16; N, ±0.14; S, ±0.27.

[b] Purified by short-path distillation into a dry ice-cooled receiver.

		C	H	N
$C_6H_9NO_2$	calc.	C 56.70	H 7.14	N 11.02
(127.1)	found	58.94	7.34	12.34

[c] Ref.[9], b.p. 114°/18 torr.

[d]

		C	H	N
$C_7H_6H_2$	calc.	C 71.19	H 5.12	N 23.72
(118.1)	found	71.42	5.37	23.65

4-Chlorophenyl 3-Methyl-3-nitrobutyl Sulfoxide (5a):

2-Nitropropane (0.89 g, 10 mmol) is added to a stirred suspension of a catalytic amount (1 mmol) of sodium hydride in dried tetrahydrofuran (30 ml) at room temperature under nitrogen. Then, 4-chlorophenyl vinyl sulfoxide (1.87 g, 10 mmol) is added to the suspension, and stirring is continued overnight. After addition of water (50 ml), the reaction mixture is extracted with diethyl ether (50 ml × 3) and dried with magnesium sulfate. The solvent is removed under reduced pressure to leave a crude product; yield: 2.69 g (85%); m.p. 123–125°.

The other sulfoxides 4 and 5 are obtained in the same manner.

1,5-Bis[4-chlorophenylsulfinyl]-3-methyl-3-nitropentane (8a):

Nitroethane (0.75 g, 10 mmol) is added to a stirred suspension of a catalytic amount (1 mmol) of sodium hydride in dried tetrahydrofuran (30 ml) at room temperature under nitrogen. Then, compound **3** (3.34 g, 20 mmol) is added to the suspension and stirring is continued overnight. The mixture is worked up as described above to give **8a** as a colorless crystalline product; yield: 3.44 g (84%); m.p. 129–131°.

Compound **8b** is obtained in a similar manner. Compound **8c** is insoluble in tetrahydrofuran and can be isolated from the reaction mixture by simple filtration.

3-Methyl-3-nitro-1-butene (6a):

4-Chlorophenyl 3-methyl-3-nitrobutyl sulfoxide (**5a**; 2.69 g, 9.8 mmol) is heated in an oil bath at 180° while the resultant product **6a** is distilled off under reduced pressure (100 torr); yield: 0.74 g (75%); b.p. 151°/760 torr.

The alkenes **6b**–**e** and **9a**–**c** are obtained in a similar manner; compound **9a** is distilled at 1 torr, compounds **6b**–**e** and **9b, c** are distilled at 14–30 torr.

2-Ethoxy-3-methyl-3-nitro-1-butene (13):

2-Nitropropane (0.89 g, 10 mmol) is added to a stirred suspension of sodium hydride (10 mmol) in dried tetrahydrofuran (30 ml) at room temperature under nitrogen. 4-Chlorophenyl 1-bromovinyl sulfoxide (2.66 g, 10 mmol) is added to the suspension and stirring is continued for 2 days. Work-up as described for **4** and **5** gives crude **11**. The crude **11** is refluxed in ethanol containing sodium ethoxide for 10 h to give **12**, which is isolated in a similar manner. Compound **12** is heated at 180° in an oil bath while the resultant product **13** is distilled off under reduced pressure (30 torr); yield: 0.28 g (19%); b.p. 172°/760 torr.

		C	H	N
$C_7H_{13}NO_3$	calc.	C 52.81	H 8.23	N 8.80
(159.2)	found	52.89	8.31	8.63

I.R. (film): ν_{max} = 2910, 1530, 1340 cm^{-1}.

^{1}H-N.M.R. (CCl$_4$, 100 MHz): δ = 1.25 (t, 3H, J = 7 Hz); 1.63 (s, 3H); 3.70 (q, 2H, J = 7 Hz); 4.08 (d, 1H, J = 3 Hz); 4.25 (d, 1H, J = 3 Hz).

Table 4. Sectral Properties of the Substituted Alkyl Aryl Sulfoxides **4** and **5**

	I.R. (film) ν_{max} [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$, 100 MHz) δ [ppm]
4a[a]	1525, 1340, 1020	1.45 (s, 3H); 1.52 (s, 3H); 2.35 (m, 4H); 7.35 (m, 5H)
5a[a]	1525, 1340, 1020	1.56 (s, 3H); 1.64 (s, 3H); 2.40 (m, 4H); 7.34 (s, 4H)
4b	1725, 1030	0.75 (t, 3H, J = 7 Hz); 1.24 (t, 6H, J = 7 Hz); 2.33 (m, 6H); 4.08 (q, 4H, J = 7 Hz); 7.34 (s, 4H)
5b	1725, 1030	0.85 (t, 3H, J = 7 Hz); 1.32 (t, 6H, J = 7 Hz); 2.35 (m, 6H); 4.13 (q, 4H, J = 7 Hz); 7.32 (q, 4H, J = 7 Hz)
5c	1745, 1725, 1020	1.24 (m, 3H); 2.30 (m, 10H); 4.12 (m, 2H); 7.50 (m, 4H)
5d	2240, 1720, 1025	1.12 (m, 6H); 1.40 (t, 3H, J = 7 Hz); 2.60 (m, 5H); 4.42 (q, 2H, J = 7 Hz); 7.80 (s, 4H)
4e	1020	2.85 (m, 4H); 7.22 (s, 5H); 7.55 (m, 5H)
5e[a]	1020	3.02 (m, 4H); 7.28 (s, 5H); 7.52 (s, 4H)
4f	1030	2.92 (t, 2H, J = 5 Hz); 3.70 (m, 2H); 4.43 (m, 2H); 7.36 (m, 10H)
5f	1030	3.00 (t, 2H, J = 5 Hz); 3.75 (m, 2H); 4.50 (m, 4H); 7.40 (m, 9H)
5g	1030	1.40 (m, 6H); 2.40 (m, 4H); 2.78 (m, 4H); 7.44 (m, 4H)

[a] I.R. (KBr).

Table 5. Spectral Properties of the Disulfinyl Compounds **8**

	I.R. (KBr) ν_{max} [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$, 100 MHz) δ [ppm]
8a	1525, 1340, 1035	1.60 (s, 3H); 2.35 (m, 8H); 7.48 (s, 8H)
8b[a]	1725, 1035	1.19 (t, 6H, J = 7 Hz); 2.40 (m, 8H); 4.12 (q, 4H, J = 7 Hz); 7.52 (s, 4H)
8c[b]	2200, 1035	2.64 (m, 8H); 7.58 (s, 8H)

[a] I.R. (film).

[b] N.M.R. (CD$_3$CN).

Table 6. Spectral Properties of the Alkenes **6** and **9**

	I.R. (film) ν_{max} [cm^{-1}]	^{1}H-N.M.R. (CCl$_4$, 100 MHz) δ [ppm]
6a	2990, 1530, 1340	1.60 (s, 3H); 5.19 (d, 2H, J = 12 Hz); 5.22 (d, 2H, J = 17 Hz); 6.07 (q, 1H, J = 12, 17 Hz)
6b	2970, 1720, 1240	0.80 (t, 3H, J = 7 Hz); 1.20 (t, 6H, J = 7 Hz); 1.96 (q, 2H, J = 7 Hz); 4.05 (q, 4H, J = 7 Hz); 4.98 (d, 2H, J = 17 Hz); 5.12 (d, 2H, J = 9 Hz); 6.13 (q, 1H, J = 9, 17 Hz)
6c	2970, 1745, 1720, 1235	1.23 (t, 3H, J = 7 Hz); 2.27 (m, 6H); 4.12 (q, 2H, J = 7 Hz); 5.10 (d, 1H, J = 18 Hz); 5.20 (d, 1H, J = 11 Hz); 6.01 (q, 1H, J = 11, 18 Hz)
6d	2970, 2245, 1735, 1235	1.00 (d, 3H, J = 6 Hz); 1.04 (d, 3H, J = 6 Hz); 1.30 (t, 3H, J = 7 Hz); 2.30 (m, 1H); 4.20 (q, 2H, J = 7 Hz); 5.39 (q, 1H, J = 5, 14 Hz); 5.86 (d, 1H, J = 5 Hz); 8.92 (d, 1H, J = 14 Hz)
6e	2960	5.10 (d, 1H, J = 16 Hz); 5.14 (d, 1H, J = 11 Hz); 6.30 (q, 1H, J = 11, 16 Hz); 7.10 (m, 5H)
9a	2995, 1540, 1340	1.80 (s, 3H); 5.30 (d, 2H, J = 18 Hz); 5.34 (d, 2H, J = 10 Hz); 6.24 (q, 2H, J = 10, 18 Hz)
9b	2980, 1725, 1250	1.25 (t, 6H, J = 6 Hz); 4.20 (q, 4H, J = 6 Hz); 5.12 (d, 2H, J = 17 Hz); 5.30 (d, 2H, J = 11 Hz); 6.30 (q, 2H, J = 11, 17 Hz)
9c	3040, 2250	5.76 (m, 6H)

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