Pergamon

Tetrahedron 57 (2001) 493–500

TETRAHEDRON

Aryl 1-chloroalkyl sulfoxides as acyl anion equivalents: a new synthesis of vinyl sulfides, ketones, and diketones from aryl 1-chloroalkyl sulfoxides and α,ω-dichloro-α,ω-disulfinylalkanes

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Received 10 October 2000; accepted 27 October 2000

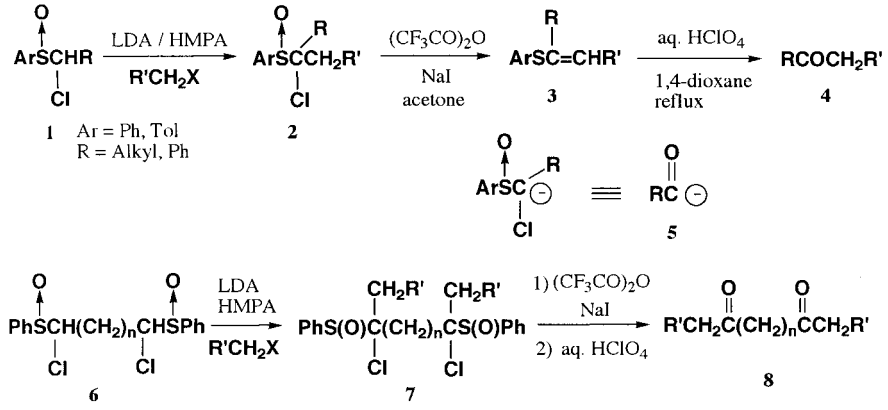
Abstract—Treatment of aryl α-chloroalkyl sulfoxides, which were synthesized from aryl 1-chloroalkyl sulfoxides by alkylation with iodoalkanes, with trifluoroacetic anhydride and NaI in acetone at low temperature afforded vinyl sulfides in high yields. The vinyl sulfides were converted to ketones by hydrolysis with $HClO_4$ in refluxing 1,4-dioxane in good yields. In this procedure, the lithiated aryl 1-chloroalkyl sulfoxides acted as acyl anion equivalents. The procedure was extended to a synthesis of α,ω-diketones starting from α,ω-dichloro-α,ω-disulfinylalkanes. The procedure was found to work well when the length of the carbon chain of the α,ω-disulfinylalkanes is longer than four, and the yields of the diketones were found to be somewhat variable (60–80%). © 2001 Elsevier Science Ltd. All rights reserved.

Ketones are obviously one of the most important compounds in organic chemistry. Among the methods for synthesizing ketones, procedures by the use of umpoled synthons[1] are quite interesting and many useful reactions have appeared. We have recently studied aryl 1-haloalkyl sulfoxides **1** in developing new synthetic methods,[2] and some novel procedures for homologation of carbonyl compounds were realized.[3] In continuation of our studies, we report herein a new method for synthesis of vinyl sulfides **3** and ketones **4** from aryl 1-chloroalkyl sulfoxides **1** and alkyl halides through aryl α-chloroalkyl sulfoxides **2**. In this sequence, the carbanion of aryl 1-chloroalkyl sulfoxides acts as acyl anion equivalents **5**. We also describe in detail the extension of this method to synthesis of diketones **8** starting from α,ω-dichloro-α,ω-disulfinylalkane **6** via **7** (Scheme 1).

1. Results and discussion

1.1. Synthesis of vinyl sulfides and ketones from aryl 1-chloroalkyl sulfoxides

The synthesis of vinyl sulfides **11** and **12**, and cyclohexyl



Scheme 1.

Keywords: aryl 1-chloroalkyl sulfoxides; acyl anion equivalents; vinyl sulfides; ketones; diketones.

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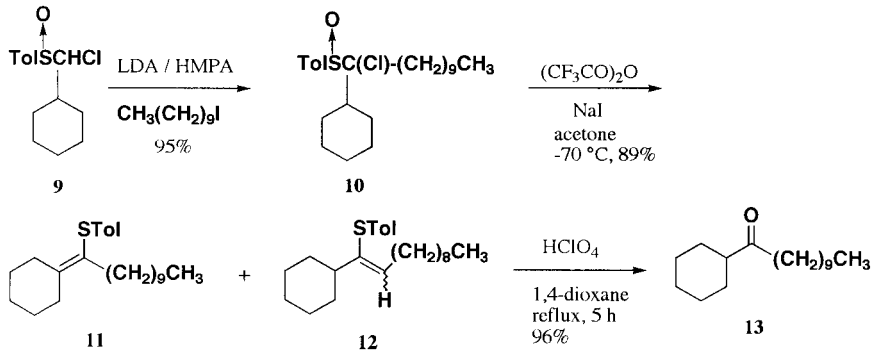
PII: S0040-4020(00)01015-2



Scheme 2.

decyl ketone (**13**) is reported as a typical example of this procedure (Scheme 2). Chloro(cyclohexyl)methyl *p*-tolyl sulfoxide (**9**)[2] was treated with LDA–HMPA in THF followed by 1-iododecane to give **10** in high yield. Next, we investigated reduction of the sulfoxide group of **10** to a sulfide group. Olah's method[4] by using $MeSiCl_3$, however, gave only a complex mixture. Reduction of the sulfoxide group of **10** with $TiCl_3$[5] did not proceed at all.

Treatment of **10** with 6 equiv. of trifluoroacetic anhydride (TFAA) in the presence of NaI (4 equiv.) in acetone at low temperature[6] gave a clean reaction mixture from which very less polar products were obtained. Detailed inspection of the mass spectra and ^1H NMR of the product suggested that the products were a mixture of unexpected vinyl sulfides **11** and **12** (89% yield; the ratio of **11**:**12**=3:7; *E*/*Z* of **12** was assigned tentatively as 2:3 from the chemical shift of the vinyl hydrogen).[7]

The presumed mechanism of this reaction is as follows (Scheme 3). Reaction of α-chloroalkyl *p*-tolyl sulfoxide **10** with TFAA gave an acyloxysulfonium ion **14**,[8] which is attacked by the iodide anion at the chlorine to give a thionium ion **15**. Elimination of the proton from **15** gives the vinyl sulfides **11** and **12**. Interestingly, the reaction of **10** with TFAA in the absence of NaI gave only a complex mixture.

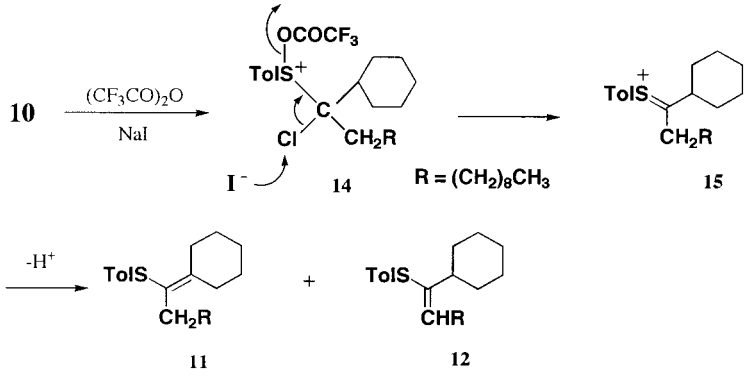
Vinyl sufides are known to be hydrolyzed to ketones under acidic conditions[6b] with a heavy metal such as mercuric chloride.[9] We investigated acid hydrolysis of the vinyl sulides **11** and **12** without the toxic mercury. Several acidic hydrolyses were studied and, finally, heating the vinyl sufides with 10% aqueous $HClO_4$ in 1,4-dioxane for 5 h was found to be the conditions of choice (Scheme 2). The conditions gave the desired ketone **13** in almost quantitative yield.

Three other aryl α-chloroalkyl sulfoxides **2** were used for studying the scope of the reaction described above, and the results are summarized in Table 1. Entries 1 and 2 show that the sulfoxides having a phenyl group as R also gave very high yields of vinyl sulfides **16** and **17**. Hydrolysis of the phenyl-substituted vinyl sulfides was found to be much slower than that of the vinyl sulfide having an alkyl group as *R*. Especially, the vinyl sulfide **17** (entry 2) was very stable under the hydrolysis conditions. In this case addition of 3 equiv. of $HgCl_2$ was found to be effective for the hydrolysis; however, the reaction was still very slow and the yield of the product, deoxybenzoin, was moderate. In a trial to synthesize a ketone without isolation of the vinyl sulfides, the experiment in entry 3 was conducted. The produced mixture of the vinyl sulfides was not purified, and the crude extract was hydrolyzed with 10% $HClO_4$ to give 89% overall yield of 6-phenyl-2-hexanone (**19**).

1.2. Synthesis of diketones from α,ω-dichloro-α,ω-disulfinylalkanes

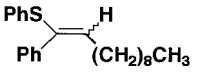
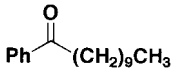
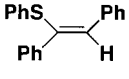
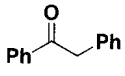
We next investigated the feasibility of the above-described procedure for the synthesis of diketones starting from α,ω-dichloro-α,ω-disulfinylalkanes **6**.

First, 1,10-di(phenylthio)decane (**20**) was synthesized from



Scheme 3.

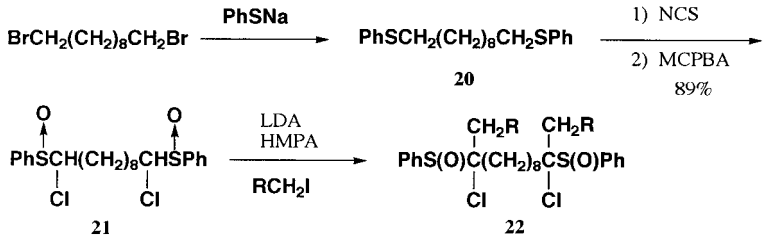
Table 1. Treatment of aryl α-chloroalkyl sulfoxides **2** with TFAA–NaI and the hydrolysis of the produced vinyl sulfides with aq. $HClO_4$

Entry	2			Vinyl sulfide	Conditions for the hydrolysis	Ketone
	Ar	R	R′	(Yield/%)[a]		(Yield/%)[a]
1	Ph	Ph	$CH_3(CH_2)_8$	 **16** (90, E/Z = 8/5)	Reflux 10 h	 **18** (98)
2	Ph	Ph	Ph	 **17** (98, *Z* only)	3 equiv. $HgCl_2$ reflux 43 h	 (68)
3	Tol	$Ph(CH_2)_4$	H	–[b]	Reflux 5 h	$Ph(CH_2)_4COCH_3$ **19** (89)[c]

[a] Isolated yield after silica gel column chromatography.
[b] Not isolated.
[c] Two-step overall yield from the aryl α-chloroalkyl sulfoxide.

1,10-dibromodecane and **20** was chlorinated with *N*-chlorosuccinimide (NCS) followed by oxidization with 3-chloroperoxybenzoic acid (MCPBA) to give 1,10-dichloro-1,10-di(phenylsulfinyl)decane (**21**) as a mixture of diastereoisomers in 98% overall yield. The chloro sulfoxide **21** was found to be a stable compound. Alkylation of **21** was conducted in the presence of HMPA as described above with several iodoalkanes to give bis-alkylated sulfoxides **22a–d** as a mixture of several diastereoisomers in 71–86% yield (Scheme 4).

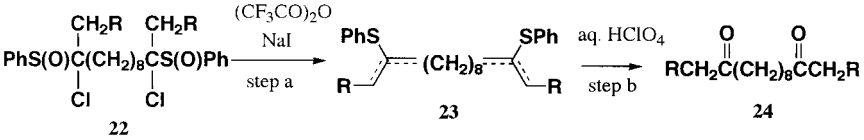
The bis-alkylated sulfoxide **22b** (see Table 2) was treated with TFAA (6 equiv.) and NaI (3 equiv.) in acetone at −55°C for 30 min. The reaction was quenched with aq.



RCH_2I R	Reaction time h	22 Yield / %	
H	2.5	**22a**	71
CH_3	3	**22b**	86
$(CH_3)_2CH$	4.7	**22c**	71
$CH_3(CH_2)_4$	2.3	**22d**	81

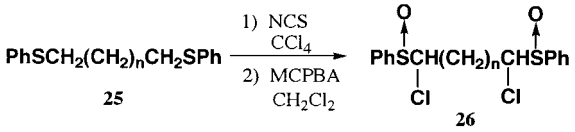
Scheme 4.

Table 2. Synthesis of diketones **24** from dichlorodisulfoxides **22**



22		Reaction time for step a	Reaction time for step b	24	
	R	h	h		Yield/%
22a	H	1.8	3	**24a**	88
22b	CH_3	1.5	1.5	**24b**	82
22c	$(CH_3)_2CH$	1.5	5	**24c**	80
22d	$CH_3(CH_2)_4$	1.5	8.5	**24d**	70

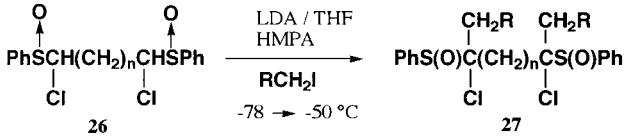
Table 3. Synthesis of α,ω-dichloro-α,ω-disulfinylalkanes **26** having various chain length



25 26

	n		Yield/%
25a	10	**26a**	98
25b	6	**26b**	81
25c	4	**26c**	85
25d	3	**26d**	94
25e	2	**26e**	77
25f	1	**26f**	76

Table 4. Alkylation of α,ω-dichloro-α,ω-disulfinylalkanes **26** with iodomethane and iodohexane



26 27

Entry	**26**	RCH_2I	Reaction time	**27**	
	n	R	h		Yield/%[a]
1	10	H[b]	1.5	**27a**	70
2	10	$CH_3(CH_2)_4$[b]	1.5	**27b**	98
3	6	H[b]	1.5	**27c**	53
4	6	$CH_3(CH_2)_4$[b]	1	**27d**	67
5	4	H[b]	1.5	**27e**	86
6	4	$CH_3(CH_2)_4$[b]	0.5	**27f**	92
7	3	H[c]	3	**27g**	13
8	3	$CH_3(CH_2)_4$[c]	3	**27h**	9
9	2	H	2.5		–[d]
10	2	$CH_3(CH_2)_4$	2.5		–[d]
11	1	H	2.5		–[d]
12	1	$CH_3(CH_2)_4$	2		–[d]

[a] Isolated yield after silica gel column chromatography.
[b] 4 equiv. of RCH_2I were used.
[c] 5 equiv. of RCH_2I were used.
[d] A complex mixture.

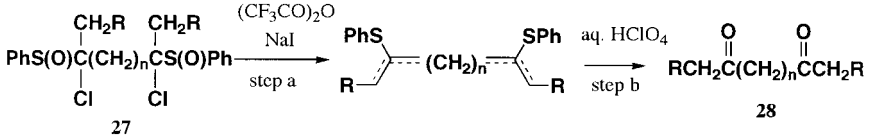
$NaHCO_3$ and aq. Na_2SO_3 as above, and the product was extracted. The ^1H NMR spectrum of the crude product showed that the product was a mixture of several isomeric vinyl sulfides **23b**. The crude products, without further purification, were hydrolyzed with 10% $HClO_4$ in 1,4-dioxane at reflux for 1.5 h to give 3,12-tetradecadione (**24b**) in 82% yield as colorless crystals (Table 2, entry 2).

Other results for the transformation of bissulfoxides **22a**, **22c**, and **22d** to the diketones **24a**, **24c**, and **24d** are summarized in Table 2. As shown in the table, 2,11-dodecanedione (**24a**) was also obtained in high overall yield (entry 1). However, in the cases of the bissulfoxides having a branched alkyl group (entry 3) or a longer alkyl chain (entry 4), the hydrolysis was found to require somewhat longer reaction time than the other two examples. Similar yields were obtained in these cases (entries 3 and 4).

We next investigated the limitation of this procedure on the length of the methylene of the α,ω-dichloro-α,ω-disulfinylalkanes **6**. First, α,ω-dichloro-α,ω-di(phenylsulfinyl)-alkanes **26a**–**26f** were synthesized from α,ω-bis(phenylthio)alkanes **25a**–**25f** in good to quantitative yields in a similar procedure as described for the synthesis of **21**. The yields are summarized in Table 3. These products **26** are a mixture of diastereoisomers and stable oily compounds.

The alkylation of the bissulfoxides **26** with LDA in THF in the presence of HMPA was carried out with two iodoalkanes, iodomethane and iodohexane, and quite interesting results were obtained (Table 4). As shown in Table 4, the alkylation of the bissulfoxide having a longer methylene chain **26a** (n=10; Table 4, entries 1 and 2) than the bissulfoxide described previously **21** (n=8) gave similar yields of the alkylated products. The bissulfoxides having a shorter methylene chain down to n=4 also gave good to excellent yields of the alkylated products (entries 3–6). However, the bissulfoxides having a much shorter methylene chain (n=2 and 1; entries 9–12) did not give the desired product but only a complex mixture. The bissulfoxide having a three-carbon methylene chain **26d** (entries 7 and 8) gave methylated products; however, the yields were very poor. The reason for these results is not clear; however, one reason for the difficulty of the alkylation must be the steric

Table 5. Synthesis of diketones **28** from dichlorodisulfinylalkanes **27** via the vinyl sulfides



27 28

Entry	**27**			Reaction time for step a	Reaction time for step b	**28**	
		R	*n*	h	h		Yield/%[a]
1	**27a**	H	10	2.5	8.5	**28a**	69
2	**27b**	$CH_3(CH_2)_4$	10	1	4	**28b**	73
3	**27c**	H	6	1.5	9	**28c**	78
4	**27d**	$CH_3(CH_2)_4$	6	1	4	**28d**	60
5	**27e**	H	4	2.5	6.5	**28e**	66
6	**27f**	$CH_3(CH_2)_4$	4	0.7	4	**28f**	69

[a] Isolated yield after silica gel column chromatography.

hindrance of the carbon bearing the chlorine and the sulfinyl group of **26d**, **26e**, and **26f**.

Finally, we investigated the conversion of the alkylated products **27a–f** to diketones **28**. The results are summarized in Table 5. The results indicate that all the alkylated bissulfoxides **27** gave moderate to good yields of diketones **28a–f**.

In conclusion, we have found that the reaction of aryl α-chloroalkyl sulfoxides with TFAA–NaI in acetone gave vinyl sulfides in good to high yields. By acidic hydrolysis of these vinyl sulfides we were able to synthesize ketones in good yields. This method was found to be applicable to synthesis of α,ω-diketones starting from α,ω-dichloro-α,ω-disulfinylalkanes.

2. Experimental

2.1. General

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 400 and 500 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel 60 (MERCK) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent, THF was distilled from benzophenone ketyl; HMPA and diisopropylamine were distilled from CaH_2. Acetone was dried over $CaSO_4$ and distilled.

2.1.1. 1-Chloro-1-cyclohexyl-1-(*p*-tolylsulfinyl)undecane (10). HMPA (0.73 ml, 4 mmol) was added to a solution of LDA (3.5 mmol) in 10 ml of dry THF at −60°C. A solution of **9** (768 mg, 2.8 mmol) in 2 ml of THF was added to the above solution dropwise with stirring. After 10 min, 1-iododecane (0.75 ml, 3.5 mmol) was added to the reaction mixture. The solution was stirred and gradually allowed to warm to −25°C for 2 h. The reaction was quenched with sat. aq. NH_4Cl and the whole was extracted with $CHCl_3$. The product was purified by silica gel column chromatography to give 1.11 g (95%) of **10** as a colorless oil. The sulfoxide **10** was a mixture of diastereoisomers and the structure was determined by disappearance of the hydrogen on the carbon bearing the sulfinyl group of **9**. Selected data are reported. IR (neat) 1082, 1060 (SO) cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J=6.3 Hz), 1.0–2.4 (29H, m), 2.44 (3H, s), 7.32 (2H, d, J=8.2 Hz), 7.65 (2H, d, J=8.2 Hz).

Other aryl α-chloroalkyl sulfoxides in Table 1 were synthesized in a similar way as described above in almost quantitative yields. Selected data are reported. 1-Chloro-1-phenyl-1-(phenylsulfinyl)undecane (entry 1): Diastereoisomeric mixture; colorless solid; IR (KBr) 1090, 1059 (SO) cm^{-1}; ^{1}H NMR δ 0.87 (3H, t, J=6.9 Hz), 1.1–1.8 (16H, m), 2.4–2.9 (2H, m), 6.9–7.4 (10H, m). 1-Chloro-1,2-diphenyl-1-(phenylsulfinyl)ethane (entry 2): See lit.[10]. 2-Chloro-6-phenyl-2-(*p*-tolylsulfinyl)hexane (entry 3): Diastereoisomeric mixture; colorless solid: IR (KBr) 1080, 1051 (SO) cm^{-1}; ^{1}H NMR δ 1.45 (3H, s), 1.5–2.7 (8H, m), 2.42 (3H, s), 7.1–7.7 (9H, m).

2.1.2. Treatment of 10 with TFAA and NaI in acetone. TFAA (0.34 ml, 2.4 mmol) was added dropwise with stirring to a suspension of the sulfoxide **10** (164 mg, 0.4 mmol) and NaI (1.6 mmol) in 4 ml of dry acetone at −55°C. The reaction mixture turned from yellow to black–green in color. The reaction mixture was stirred at −55°C for 1 h. To the reaction mixture were added sat. aq. $NaHCO_3$ (4 ml) and sat. aq. Na_2SO_3 (4 ml). The whole was extracted with ether–benzene. The product was purified by silica gel column chromatography to give 128 mg (89%) of a mixture of the vinyl sulfide **11** and **12** as colorless oil. IR (neat) 1491, 1448, 804 cm^{-1}; ^{1}H NMR δ 0.88 (3H, CH_3), 2.29, 2.31 (CH_3), 5.51 (vinyl-H, t, J=7.3 Hz), 5.92 (vinyl-H, t, J=6.9 Hz). MS m/z (%) 358 (M^+, 100), 267 (13), 245 (27). Calcd for $C_{24}H_{38}S$: M, 358.2693. Found: m/z 358.2699.

2.1.3. 1-Phenyl-1-phenylthio-1-undecene (16). Colorless oil (*E*/*Z*-mixture); IR (neat) 1477, 1439, 739 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J=6.9 Hz), 1.1–1.6 (14H, m), 2.13 (q, J= 7.3 Hz), 2.53 (q, J=7.3 Hz), 6.14 (t, J=7.2 Hz), 6.43 (t, J=7.2Hz), 7.0–7.6 (10H, m). MS m/z (%) 338 (M^+, 28), 225 (26), 218 (29), 105 (100). Calcd for $C_{23}H_{30}S$: M, 338.2065. Found: m/z 338.2046.

2.1.4. 1,2-Diphenyl-1-phenylthioethene (17). Colorless solid; IR (KBr) 1579, 1477, 1439, 739, 692 cm^{-1}; ^{1}H NMR δ 6.79 (1H, s), 6.9–7.7 (15H, m). MS m/z (%) 288 (M^+, 96), 210 (8), 179 (87), 178 (100). Calcd for $C_{20}H_{16}S$: M, 288.0928. Found: m/z 288.0936.

2.1.5. Cyclohexyl decyl ketone (13). 10% Aqueous perchloric acid (1 ml) was added to a solution of the mixture of the vinyl sulfides **11** and **12** (108 mg, 0.3 mmol) in 5 ml of 1,4-dioxane and the reaction mixture was heated under reflux for 5 h. Sat. aq. $NaHCO_3$ (2 ml) was added to the reaction mixture and the whole was extracted with hexane. The organic layer was washed once with sat. aq. NH_4Cl and dried over $MgSO_4$. The product was purified by silica gel column chromatography to give 68 mg (96%) of the ketone **13** as colorless oil. IR (neat) 1709 (CO), 1450, 1375 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J=6.9 Hz), 1.2–1.9 (24H, m), 2.32 (1H, m), 2.41 (2H, t, J=7.3 Hz). MS m/z (%) 252 (M^+, 16), 169 (48), 126 (36), 111 (45), 83 (100). Calcd for $C_{17}H_{32}O$: M, 252.2451. Found: m/z 252.2438.

2.1.6. 1-Phenyl-1-undecanone (18).[11] Colorless oil; IR (neat) 1687 (CO), 1448, 690 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J=6.9 Hz), 1.26 (14H, m), 1.73 (2H, m), 2.59 (2H, t, J= 7.6 Hz), 7.2–8.0 (5H, m).

2.1.7. 6-Phenyl-2-hexanone (19).[12] Colorless oil; IR (neat) 1716 (CO), 1454, 1360, 700 cm^{-1}; ^{1}H NMR δ 1.62 (4H, m), 2.11 (3H, s), 2.44, 2.61 (each 2H, m), 7.1–7.5 (5H, m). MS m/z (%) 176 (M^+, 73), 158 (12), 129 (26), 118 (87), 91 (100).

2.1.8. 1,10-Di(phenylthio)decane (20). Benzenethiol (3.5 ml, 32 mmol) was added to a solution of sodium ethoxide (32 mmol) in 90 ml of ethanol. To this solution was added dropwise a solution of 1,10-dibromodecane (4.50 g, 15 mmol)

in ethanol and the reaction mixture was stirred at room temperature for 45 min. The ethanol was evaporated and to the residue was added water. The whole was extracted with a mixture of ether–benzene. The organic layer was washed successively with 5% NaOH and sat. aq. NH_4Cl. The solution was dried over $MgSO_4$ and the solvent was evaporated to give a crystalline residue, which was recrystallized from AcOEt–hexane to give **20** (5.35 g, 91%) as colorless crystals; mp 87–88°C. IR (KBr) 1580, 1479, 1438, 732 cm^{-1}; ^1H NMR δ 1.2–1.5 (12H, m), 1.63 (4H, m), 2.91 (4H, t, J=7.3 Hz), 7.1–7.4 (10H, m). MS m/z (%) 358 (M^+, 100), 249 (12), 123 (34), 110 (42). Calcd for $C_{22}H_{30}S_2$: M, 358.1787. Found: m/z 358.1786. Anal Calcd: C, 73.68; H, 8.43; S, 17.88. Found: C, 73.48; H, 8.48; S, 18.17.

2.1.9. 1,10-Dichloro-1,10-di(phenylsulfinyl)decane (21). *N*-Chlorosuccinimide (purified by recrystallization from benzene; 0.59 g, 4.4 mmol) was added to a solution of **20** (0.72 g, 2 mmol) in carbon tetrachloride (40 ml). The suspension was stirred at room temperature for 2.5 h. The precipitates were filtered off and the solvent of the filtrate was evaporated. The residue was dissolved with CH_2Cl_2 (70 ml) and the solution was cooled to −60°C. To the solution was added MCPBA (0.77 g, 4.4 mmol) portionwise with stirring and the reaction mixture was stirred at −60°C for 2 h. The solution was washed twice with 5% NaOH followed by sat. aq. NH_4Cl. The solution was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by silica gel column chromatography to give 900 mg (98%) of **21** (diastereoisomeric mixture) as colorless oil. IR (neat) 1444, 1086, 1052 (SO), 751 cm^{-1}; ^1H NMR δ 1.2–1.8 (12H, m), 1.96 (2H, m), 2.23 (2H, m), 4,40 (1.5H, dd, J=9.7, 2.7 Hz), 4.53 (0.5H, dd, J=9.1, 4.0 Hz), 7.5–7.8 (10H, m). MS m/z (%) 458 (M^+, trace), 442 (trace), 333 (17), 126 (100). Calcd for $C_{22}H_{28}Cl_2O_2S_2$: M, 458.0908. Found: m/z 458.0899.

2.1.10. 3,12-Dichloro-3,12-di(phenylsulfinyl)tetradecane (22b). To a solution of LDA (1.5 mmol) in 10 ml of THF at −78°C was added dropwise with stirring a solution of **21** (230 mg, 0.5 mmol) in THF followed by HMPA (0.26 ml, 1.5 mmol). The reaction mixture was stirred for 10 min, then iodoethane (0.16 ml, 2 mmol) was added and the solution was stirred and allowed to warm to −50°C for 3 h. The reaction was quenched by sat. aq. NH_4Cl and the whole was extracted with ether–benzene. The solution was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by silica gel column chromatography to give 204 mg (86%) of **22b** (diastereoisomeric mixture) as light yellow oil. IR (neat) 1444, 1082, 1049 (SO), 750 cm^{-1}; ^1H NMR δ 1.01 (6H, CH_3), 1.1–1.9 (14H, m), 1.9–2.3 (6H, m), 7.4–7.8 (10H, m). MS m/z (%) 514 (M^+, trace), 262 (6), 126 (100).

2.1.11. α,ω-Dichloro-α,ω-di(phenylsulfinyl)alkanes (22a, 22c, and 22d). These alkylated chloro sulfoxides were synthesized from **21** in a similar way as described above. These products are a mixture of several diastereoisomers, and it was found difficult to obtain the data for high-resolution mass spectra. 2,11-Dichloro-2,11-di(phenylsulfinyl)dodecane (**22a**). Colorless oil; IR (neat) 1444, 1082, 1052 (SO), 749 cm^{-1}; ^1H NMR δ 1.2–1.8 (19H, m), 2.0–2.2 (3H, m), 7.5–7.6 (6H, m), 7.7–7.8 (4H, m). MS m/z (%) 488 (M^+, trace), 126 (100). 4,13-Dichloro-2,15-dimethyl-4,13-di-(phenylsulfinyl)hexadecane (**22c**). Colorless oil; IR (neat) 1444, 1082, 1052, 749 cm^{-1}; ^1H NMR δ 1.0–2.1 (34H, m),7.5–7.8 (10H). MS m/z (%) 572 (M^+, trace), 143 (100), 126 (78). 7,16-Dichloro-7,16-di(phenylsulfinyl)-docosane (**22d**). Colorless oil; IR (neat) 1444, 1082, 1052, 749 cm^{-1}; ^1H NMR δ 0.8–0.9 (6H, m), 1.2–1.7 (30H, m), 1.9–2.2 (6H, m), 7.5–7.8 (10H, m). MS m/z (%) 626 (M^+, trace), 531 (87), 125 (26).

2.1.12. 3,12-Tetradecanedione (24b). TFAA (0.17 ml, 1.2 mmol) was added dropwise with stirring to a suspension of the sulfoxide **22b** (51.6 mg, 0.1 mmol) and NaI (0.09 g, 0.6 mmol) in 3 ml of dry acetone at −55°C. The reaction mixture turned from yellow to black–green in color. The reaction mixture was stirred at −55°C for 1.5 h. To the reaction mixture were added sat. aq. $NaHCO_3$ and sat. aq. Na_2SO_3. The whole was extracted with ether–benzene. The organic layer was washed with sat. aq. NH_4Cl and dried over $MgSO_4$. The solvent was evaporated to give a residue, which was used in the next reaction without further purification. 10% aqueous perchloric acid (1 ml) was added to a solution of the mixture of the product (vinyl sulfides **23**) in 5 ml of 1,4-dioxane and the reaction mixture was heated under reflux for 1.5 h. Sat. aq. $NaHCO_3$ was added to the reaction mixture and the whole was extracted with ether–benzene. The solution was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by silica gel column chromatography to give 19.2 mg (82%) of the ketone **24b** as colorless crystals. Mp 71.5–72°C (AcOEt–hexane). IR (KBr) 1710, 1701 (CO), 1376, 1116 cm^{-1}; ^1H NMR δ 1.05 (6H, t, J=7.2 Hz), 1.28 (8H, m), 1.56 (4H, m), 2.37–2.44 (8H, m). MS m/z (%) 226 (M^+, 3), 197 (17), 57 (100). Calcd for $C_{14}H_{26}O_2$: M,226.1931. Found: m/z 226.1931. Anal Calcd: C, 74.29; H, 11.58. Found: C, 74.56; H, 11.63.

2.1.13. 2,11-Dodecanedione (24a). Colorless crystals; mp 66–67°C (H_2O). IR (KBr) 1701 (CO), 1560, 1363 cm^{-1}; ^1H NMR δ 1.28 (8H, m), 1.53–1.59 (4H, m), 2.13 (6H, s), 2.41 (4H, t, J=7.3 Hz). MS m/z (%) 198 (M^+, trace), 183 (trace), 141 (10), 123 (12), 43 (100). Calcd for $C_{12}H_{22}O_2$: M, 198,1618. Found: m/z 198,1614. Anal Calcd: C, 72.68; H, 11.18. Found: C, 72.45; H, 10.92.

2.1.14. 2,15-Dimethyl-4,13-hexadecanedione (24c). Colorless oil; IR (neat) 1702 (CO), 1466, 1411 cm^{-1}; ^1H NMR δ 0.90 (12H, d, J=6.6 Hz), 1.27 (8H, m), 1.55 (4H, quint, J=7.1 Hz). 2.13 (2H, septet, J=6.8 Hz), 2.27 (4H, d, J=6.8 Hz) 2.36 (4H, t, J=7.1 Hz). MS m/z (%) 282 (M^+, 7), 225 (17), 183 (52), 85 (100). Calcd for $C_{18}H_{34}O_2$: M, 282.2556. Found: m/z 282.2553.

2.1.15. 7,16-Docosanedione (24d). Colorless crystals; mp 86–87°C (hexane). IR (KBr) 1700 (CO), 1654, 1543 cm^{-1}; ^1H NMR δ 0.88 (6H, t, J=6.6 Hz), 1.27 (20H, m), 1.5–1.6 (8H, m), 2.38 (8H, t, J=6.9Hz). MS m/z (%) 338 (M^+, 5), 253 (21), 211 (94), 113 (95), 43 (100). Calcd for $C_{22}H_{42}O_2$: M, 338.3177. Found: m/z 338.3182. Anal Calcd: C, 78.04; H, 12.50. Found: C, 77.78; H, 12.21.

2.1.16. 1,12-Dichloro-1,12-di(phenylsulfinyl)dodecane (26a). Colorless oil; IR (neat) 1444, 1087, 1052 (SO), 750 cm^{-1}; ^1H NMR δ 1.3–1.7 (16H, m), 1.9–2.0 (2H, m),

2.2–2.3 (2H, m), 4.41 (1.5H, dd, J=9.8, 2.8 Hz), 4.53 (0.5H, dd, J=9.1, 4.1 Hz), 7.5–7.8 (10H, m). MS m/z (%) 361 ([M−PhSO]$^+$, 8), 126 (100).

2.1.17. 1,8-Dichloro-1,8-di(phenylsulfinyl)octane (26b). Colorless oil; IR (neat) 1444, 1087, 1052 (SO), 756 cm^{-1}; ^{1}H NMR δ 1.2–1.7 (8H, m), 1.96 (2H, m), 2.23 (2H, m), 4.40 (1.5H, m), 4.5–4.6 (0.5H, m), 7.5–7.8 (10H, m). MS m/z (%) 431 ([M+H]$^+$, trace), 305 (21), 126 (100). Calcd for $C_{20}H_{25}Cl_2O_2S_2$: [M+H], 431.0687. Found: m/z 431.0662.

2.1.18. 1,6-Dichloro-1,6-di(phenylsulfinyl)hexane (26c). Colorless oil; IR (neat) 1440, 1086, 1047 (SO), 745 cm^{-1}; ^{1}H NMR δ 1.6–2.3 (8H, m), 4.39 (1.5H, m), 4.5–4.6 (0.5H, m), 7.5–7.8 (10H, m). MS m/z (%) 403 ([M+H]$^+$, trace), 277 (12), 126 (100), 78 (100). Calcd for $C_{18}H_{21}Cl_2O_2S_2$: [M+H], 403.0360. Found: m/z 403.0375.

2.1.19. 1,5-Dichloro-1,5-di(phenylsulfinyl)pentane (26d). Colorless oil; IR (neat) 1444, 1088, 1051 (SO), 752 cm^{-1}; ^{1}H NMR δ 1.6–1.9 (2H, m), 2.0–2.2 (2H, m), 2.30 (2H, m), 4.3–4.4 (1.5H, m), 4.5–4.6 (0.5H, m), 7.5–7.8 (10H, m). MS m/z (%) 388 (M$^+$, trace), 263 (18), 126 (100). Calcd for $C_{17}H_{18}Cl_2O_2S_2$: M, 388.0125. Found: m/z 388.0132.

2.1.20. 1,4-Dichloro-1,4-di(phenylsulfinyl)butane (26e). A mixture of colorless oil and crystals; IR (neat) 1443, 1086, 1045 (SO), 748 cm^{-1}; ^{1}H NMR δ 2.1–2.2 (1H, m), 2.3–2.5 (2H, m), 2.6–2.7 (1H, m), 4,4–4.7 (2H, m), 7.5–7.8 (10H, m). MS m/z (%) 374 (M$^+$, 2), 249 (91), 125 (89), 109 (100). Calcd for $C_{16}H_{16}Cl_2O_2S_2$: M, 373.9969. Found: m/z 373.9971.

2.1.21. 1,3-Dichloro-1,3-di(phenylsulfinyl)propane (26f). Colorless oil; IR (neat) 1444, 1087, 1045 (SO), 744 cm^{-1}; ^{1}H NMR δ 2.3–2.4 (1H, ddd, J=14.5, 11.5, 2.8 Hz), 2.7–2.8 (1H, ddd, J=13.9, 11.3, 2.8 Hz), 4.6–4.7 (1H, dd, J=11.3, 2.8 Hz), 4.8–4.9 (1H, dd, J=11.3, 2.8 Hz), 7.5–7.7 (10H, m). MS m/z (%) 360 (M$^+$, trace), 235 (11), 125 (91), 109 (100). Calcd for $C_{15}H_{14}Cl_2O_2S_2$: M, 359.9812. Found: m/z 359.9820.

2.1.22. α,ω-Dichloro-α,ω-di(phenylsulfinyl)alkanes (27a–27h). Similar to the sulfoxides **22**, these sulfoxides are a mixture of several diastereoisomers, and it was difficult to obtain the data for mass spectrum. 2,13-Dichloro-2,13-di(phenylsulfinyl)tetradecane (**27a**). Light yellow oil. IR (neat) 1444, 1085, 1051 (SO), 750 cm^{-1}; ^{1}H NMR δ 1.2–1.8 (22H, m), 2.0–2.2 (4H, m), 7.5–7.6 (6H, m), 7.7–7.8 (4H, m). MS m/z (%) 126 (100). 7,18-Dichloro-7,18-di(phenylsulfinyl)tetracosane (**27b**). Light yellow oil. IR (neat) 1444, 1082, 1052 (SO), 749 cm^{-1}; ^{1}H NMR δ 0.8–1.7 (40H, m), 1.9–2.2 (6H, m), 7.5–7.8 (10H, m). MS m/z (%) 402 (100), 126 (47). 2,9-Dichloro-2,9-di(phenylsulfinyl)decane (**27c**). Colorless oil. IR (neat) 1444, 1088, 1054 (SO), 747 cm^{-1}; ^{1}H NMR δ 1.2–1.8 (16H, m), 2.0–2.2 (2H, m), 7.5–7.6 (6H, m), 7.7–7.8 (4H, m). MS m/z (%) 126 (100), 78 (50). 7,14-Dichloro-7,14-di(phenylsulfinyl)eicosane (**27d**). Colorless oil. IR (neat) 1444, 1088, 1054 (SO), 747 cm^{-1}; ^{1}H NMR δ 0.8–0.9 (6H, m), 1.2–1.7 (26H, m), 1.9–2.1 (6H, m), 7.5–7.8 (10H, m). MS m/z (%) 346 (17), 126 (100). 2,7-Dichloro-2,7-di(phenylsulfinyl)octane (**27e**). Colorless oil. IR (neat) 1444, 1085, 1049 (SO), 750 cm^{-1}; ^{1}H NMR δ 1.4–2.2 (14H, m), 7.5–7.8 (10H, m). MS m/z (%) 430 (M$^+$, trace), 305 (11), 143 (100). 7,12-Dichloro-7,12-di(phenylsulfinyl)octadecane (**27f**). Colorless oil. IR (neat) 1443, 1082, 1051 (SO), 749 cm^{-1}; ^{1}H NMR δ 0.8–0.9 (6H, t, J=7 Hz), 1.2–1.8 (22H, m), 1.9–2.2 (6H, m), 7.5–7.6 (6H, m), 7.7–7.8 (4H, m). MS m/z (%) 318 (10), 283 (6), 126 (98), 78 (100). 2,6-Dichloro-2,6-di(phenylsulfinyl)heptane (**27g**). Colorless oil. IR (neat) 1444, 1091, 1051 (SO), 746 cm^{-1}; ^{1}H NMR δ 1.2–2.5 (12H, m), 7.5–7.9 (10H, m). MS m/z (%) 302 (7), 250 (16), 126 (84). 7,12-Dichloro-7,12-di(phenylsulfinyl)-octadecane (**27h**). Colorless oil. IR (neat) 1443, 1083, 1053 (SO), 749 cm^{-1}; ^{1}H NMR δ 0.8–0.9 (6H, m), 1.2–2.5 (26H, m), 7.3–7.8 (10H, m). MS m/z (%) 290 (18), 126 (100).

2.1.23. 2,13-Tetradecanedione (28a). Colorless crystals; mp 73–74°C (hexane). IR (KBr) 1715, 1701 (CO), 1379, 1165 cm^{-1}; ^{1}H NMR δ 1.27 (12H, m), 1.57 (4H, m), 2.13 (6H, s). 2.42 (4H, t, J=7.5 Hz). MS m/z (%) 226 (M$^+$, 3), 211 (2), 169 (12), 151 (10), 43 (100). Calcd for $C_{14}H_{26}O_2$: M, 226.1931. Found: m/z 226.1928. Anal Calcd: C, 74.29; H, 11.58. Found: C, 73.97; H, 11.38.

2.1.24. 7,18-Tetracosanedione (28b). Colorless crystals; mp 89–90°C (hexane). IR (KBr) 1705, 1699 (CO), 1458, 1381 cm^{-1}; ^{1}H NMR δ 0.88 (6H, m), 1.29 (24H, m), 1.52–1.57 (8H, m), 2.38 (4H, t, J=7.5 Hz), 2.39 (4H, t, J=7.5 Hz). MS m/z (%) 366 (M$^+$, 29), 296 (27), 239 (100), 113 (88). Calcd for $C_{24}H_{46}O_2$: M, 366.3496. Found: m/z 366.3502. Anal Calcd: C, 78.61; H, 12.64. Found: C, 78.39; H, 12.62.

2.1.25. 2,9-Decanedione (28c). Colorless crystals; mp 53–54°C (hexane). IR (KBr) 1715, 1702 (CO), 1375, 1163 cm^{-1}; ^{1}H NMR δ 1.30 (4H, m), 1.54–1.60 (4H, m), 2.13 (6H, s), 2.42 (4H, t, J=7.3 Hz). MS m/z (%) 170 (M$^+$, trace), 152 (8), 113 (20). Calcd for $C_{10}H_{18}O_2$: M, 170.1306. Found: m/z 170.1310. Anal Calcd: C, 70.55; H, 10.66. Found: C, 70.13; H, 10.34.

2.1.26. 7,14-Eicosanedione (28d). Colorless crystals; mp 83–84°C (hexane). IR (KBr) 1698 (CO), 1420, 1382 cm^{-1}; ^{1}H NMR δ 0.88 (6H, t, J=6.4 Hz), 1.27 (16H, m), 1.53–1.58 (8H, m), 2.38 (8H, t, J=7.3 Hz). MS m/z (%) 310 (M$^+$, 18), 225 (30), 183 (100). Calcd for $C_{20}H_{38}O_2$: M, 310.2869. Found: m/z 310.2856. Anal Calcd: C, 77.36; H, 12.34. Found: C, 77.09; H, 12.36.

2.1.27. 2,7-Octanedione (28e). Colorless oil; IR (neat) 1717, 1700 (CO) cm^{-1}; ^{1}H NMR δ 1.56 (4H, m), 2.14 (6H, s), 2.45 (4H, t, J=6.7 Hz). MS m/z (%) 142 (M$^+$, 0.6), 124 (0.6), 84 (32), 43 (100). Calcd for $C_8H_{14}O_2$: M, 142.0994. Found: m/z 142.0990.

2.1.28. 7,12-Octadecanedione (28f). Colorless crystals; mp 75–76°C (hexane). IR (KBr) 1700 (CO), 1684, 1466 cm^{-1}; ^{1}H NMR δ 0.88 (6H, t, J=6.8 Hz), 1.25–1.32 (12H, m), 1.51–1.58 (8H, m), 2.33–2.43 (8H, m). MS m/z (%) 282 (M$^+$, 3), 264 (12), 212 (20), 176 (60), 113 (89), 34 (100). Calcd for $C_{18}H_{34}O_2$: M, 282.2565. Found: m/z 282.2557. Anal Calcd: C, 76.60; H, 12.14. Found: C, 76.29; H, 11.84.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research No. 11640545 from the Ministry of Education, Science, Sports, and Culture, which is gratefully acknowledged.

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