mmol) were heated at 58 °C in THF (20 mL) and $CHCl_3$ (10 mL) for 22 h (hood). Removal of solvent and then silica gel chromatography ($CHCl_3$ then 10% $CH_3OH/CHCl_3$) gave 0.36 g (98%) of white solid, which was recrystallized from EtOAc, to furnish 0.211 g (59%) **14**: mp 140–141 °C; ^1H NMR δ 1.2–1.8 (m, 8 H), 2.21 (t, 2 H), 3.43 (q, 2 H), 5.13 and 5.19 (2 s, 4 H), 5.5 (br s, 2 H), 7.25–7.5 (m, 10 H), 8.33 (br s, 1 H), 11.77 (br s, 1 H). Anal. Calcd for $C_{24}H_{30}N_4O_5$: C, 63.42; H, 6.65; N, 12.33. Found: C, 63.22; H, 6.72; N, 12.26.

ω-Bis(benzyloxycarbonyl)guanidino α-(Methoxymethyl ester) 16. Methyl glyoxalate[19] (79.2 mg, 0.899 mmol) and **14** (0.288 g, 0.634 mmol) were heated at 40 °C in THF (6 mL) for 38 h. Solvent removal in vacuo afforded crude **15**. Alcohol **15** was stirred (room temperature, Ar) in 0.31 M H_2SO_4 in CH_3OH (10 mL) for 18 h. The solution was poured into cold, dilute $NaHCO_3$ (50 mL) and extracted with ether (4 × 50 mL). After washing with water (3×) and brine, the crude product was chromatographed on a column (silica gel, 3% $EtOH/CHCl_3$) to give 242 mg (68%) of **16**: ^1H NMR δ 1.25–1.8 (m, 8 H), 2.30 (t, 2 H), 3.35–3.55 (q + s, 5 H), 3.82 (s, 3 H), 5.15 and 5.22 (2 s, 4 H), 5.58 (d, J = 9, 1 H, collapses to a singlet with D_2O), 6.5 (br, 1 H), 7.3–7.5 (m, 10 H), 8.3 (br s, 1 H), 11.77 (br s, 1 H). Anal. Calcd for $C_{28}H_{36}N_4O_8$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.23; H, 6.60; N, 9.97.

Pentaprotected Deoxyspergualin 17. Ester **16** (199 mg, 0.358 mmol) and amine **12** (138 mg, 0.399 mmol) were heated in benzene (0.7 mL) at 40 °C for 36 h. Preparative layer chromatography (4% $EtOH/CHCl_3$) gave 167 mg of **17** (54%): ^1H NMR δ 1.2–1.8 (m, 32 H), 2.30 (t, 2 H), 3.0–3.5 (m + s, 13 H), 5.1 (br s, 1 H), 5.13 and 5.19 (2 s, 4 H), 5.50 (d, 1 H, J = 9), 6.9 (br s, 2 H), 7.25–7.5 (m, 10 H), 8.35 (br s, 1 H), 11.8 (br s, 1 H). Anal. Calcd for $C_{44}H_{67}N_7O_{11}\cdot H_2O$: C, 59.51; H, 7.83; N, 11.04. Found: C, 59.21; H, 7.86; N, 10.81.

***N,N'*-Bis(*tert*-butoxycarbonyl)-*S*-methoxyisothiourea (18).** Di-*tert*-butyl dicarbonate (5.81 g, 26.6 mmol) and *S*-methylisothiourea·$^1/_2H_2SO_4$ (2.53 g, 18.2 mmol) were vigorously stirred in a biphasic system, CH_2Cl_2 (50 mL) and saturated $NaHCO_3$ (50 mL), for 1.6 days. Layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (2×). After water washing, the crude product contained BOC_2O and was taken up in CH_2Cl_2 (50 mL) and saturated $NaHCO_3$ (50 mL) and stirred with *S*-methylisothiourea·$^1/_2H_2SO_4$ (0.55 g, 3.95 mmol) for 2–3 days and worked up as before. Elution with 15% hexane/$CHCl_3$ and then $CHCl_3$ through a silica gel column afforded 3.46 g (90%) of white solid: mp 122–123 °C; ^1H NMR δ 1.53 (s, 18 H), 2.40 (s, 3 H), 11.63 (br s, 1 H); IR ($CHCl_3$) 3200, 1750 cm^{-1}. Anal. Calcd for $C_{12}H_{22}N_2O_4S$: C, 49.63; H, 7.64; N, 9.65; S, 11.04. Found: C, 49.56; H, 7.68; N, 9.63; S, 11.00.

7-[N^2,N^3-Bis(*tert*-butoxycarbonyl)guanidino]heptanamide (19). Reagent **18** (2.09 g, 7.20 mmol) and 7-aminoheptanamide[14] (0.988 g, 6.85 mmol) were heated at 52 °C for 3 h in THF (52 mL) and water (1 mL) (hood). Solvent was removed, and the residue was treated with 5% $NaHCO_3$, followed by extraction with $CHCl_3$ (2×). After a water wash, the crude product was chromatographed on silica gel (10:45:45 $EtOH/EtOAc/CHCl_3$) to give 1.88 g (71%) of **19**: ^1H NMR δ 1.3–1.8 (m, 26 H), 2.24 (t, 2 H), 3.42 (q, 2 H), 5.5 (br s, 2 H), 8.3 (br s, 1 H), 11.53 (br s, 1 H); IR ($CHCl_3$) 3680, 3540, 3420, 3340, 1725, 1685 cm^{-1}. Anal. Calcd for $C_{18}H_{34}N_4O_5$: C, 55.94; H, 8.87; N, 14.50. Found: C, 55.67; H, 8.86; N, 14.42.

Silylated Bis(*tert*-butoxycarbonyl)guanidine Methyl Ester (21). A solution of amide **19** (0.391 g, 1.01 mmol) and methyl glyoxalate (0.112 g, 1.27 mmol) in THF was heated at 42 °C for 15 h. After solvent removal, imidazole (0.22 g, 3.23 mmol), *tert*-butyldimethylsilyl chloride (0.21 g, 1.39 mmol), and dry DMF (1.0 mL) were added to the intermediate **20**. The solution was stirred for 2 days (room temperature, N_2) and then quenched with water. Ether extraction (5×), followed by water washing (3×), and then brine gave 0.49 g of product. Column chromatography (SiO_2, 5% $EtOAc/CHCl_3$) and then preparative TLC (SiO_2, 4% $EtOAc/CHCl_3$) on a portion of the resulting product furnished 0.201 g of **21** (34% yield): ^1H NMR δ 0.13 and 0.19 (2 s, 6 H), 0.90 (s, 9 H), 1.25–1.8 (m and s, 26 H), 2.24 (t, 2 H), 3.42 (q, 2 H), 3.79 (s, 3 H), 5.84 (d, 1 H, J = 10), 6.54 (br d, 1 H), 8.35 (br s, 1 H), 11.51 (br s, 1 H); IR ($CHCl_3$) 3440, 3340, 1750, 1725, 1690, 1630 cm^{-1}. Anal. Calcd for $C_{27}H_{52}N_4O_8Si$: C, 55.08; H, 8.90; N, 9.52. Found: C, 55.22; H, 8.91; N, 9.47.

Pentakis(*tert*-butoxycarbonyl)-11-silyl-15-deoxyspergualin 22. Ester **21** (158 mg, 0.268 mmol) and N^1,N^4-bis(*tert*-butoxycarbonyl)spermidine (**12**) (102.7 mg, 0.297 mmol) were stirred in benzene (0.5 mL) (Ar) for 46 h at 38 °C. After solvent removal, purification of the crude product by preparative TLC (2:24:74 $EtOH/EtOAc/CHCl_3$) gave 114 mg (47%) of **22**: ^1H NMR δ 0.10 and 0.20 (2 s, 6 H), 0.91 (s, 9 H), 1.2–2.0 (m, 50 H), 2.23 (t, 2 H), 3.0–3.6 (m, 10 H), 5.74 (d, J = 9, 1 H), 6.7 (br s, 2 H), 8.3 (br s, 1 H), 11.53 (br s, 1 H). Anal. Calcd for $C_{43}H_{83}N_7O_{11}Si$: C, 57.24; H, 9.27; N, 10.87. Found: C, 57.08; H, 9.33; N, 10.83.

(±)-15-Deoxyspergualin (2b). To **22** (23 mg, 0.025 mmol) was added trifluoroacetic acid (2 mL). After stirring for 43 min (room temperature, Drierite), excess solvent was removed under a stream of nitrogen, and the residue was dried in vacuo (P_2O_5). Purification was carried out following the literature.[8] First, CM-Sephadex Cation Exchanger (4.06 g), equilibrated in water, was used, eluting with water and 0.2 N, 0.4 N, 0.6 N, 0.8 N (50 mL each), and then 1.0 N aqueous NaCl. Fractions 17–21 (ninhydrin active) were combined and lyophilized, stirred with CH_3OH, and filtered. Next a column of Sephadex LH-20-100 (8.54 g), preswelled in CH_3OH was used (acid-washed glassware). Elution with methanol gave 9 mg of (±)-15-deoxyspergualin (71%): ^1H NMR (300 MHz, D_2O) δ 5.46 (s, 1 H), 3.30 (t, 2 H), 3.05–3.25 (m, 8 H), 2.31 (t, 2 H), 2.10 (quintet, 2 H), 1.55–1.8 (m, 8 H), 1.33–1.45 (m, 4 H), 4.80, HOD. This 300-MHz spectrum was identical with that of a known sample of **2b**.[24] The two samples were identical by cospotting on silica gel TLC (3:2:2:1 1-butanol/pyridine/water/acetic acid).[3]

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A Regioselective Synthesis of Cyclopentenones from 4-Thianone

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Alkyl-substituted 3-cyclopentenones **4** and **5** were prepared in moderate to good yields starting from 4-thianone by the selective alkylation and Ramberg–Bäcklund-type reactions. One route starts with 6-alkyl-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-dioxides (**8**) and another with 7-alkyl-1,4-dioxa-7-(*p*-tolylsulfonyl)-8-thiaspiro[4.5]decane 8,8-dioxides (**15**), followed by acid-catalyzed cleavage of the 1,3-dioxolane ring of 1,4-dioxaspiro[4.4]non-7-enes **9** and **16** to afford **4** and **5**.

Considerable attention has been focused in recent years on cyclic sulfur compounds for the synthesis of interesting compounds.[1] 4-Thianone (**1**) is a heterocyclic compound consisted of five carbon units and a sulfur atom as an

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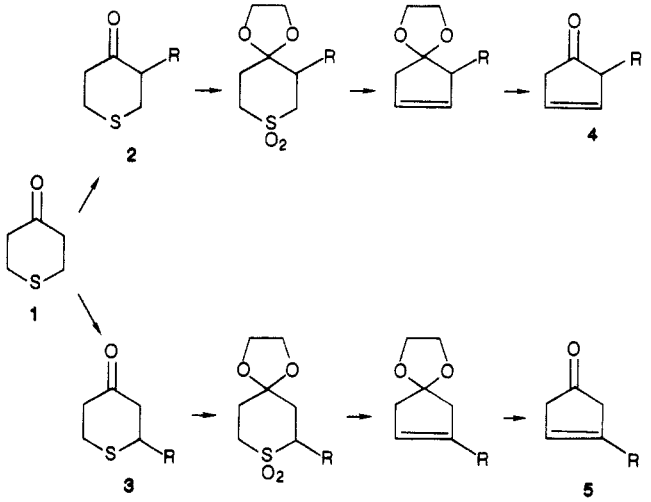
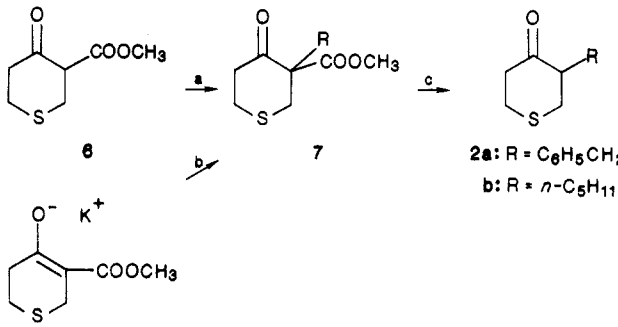
Scheme I



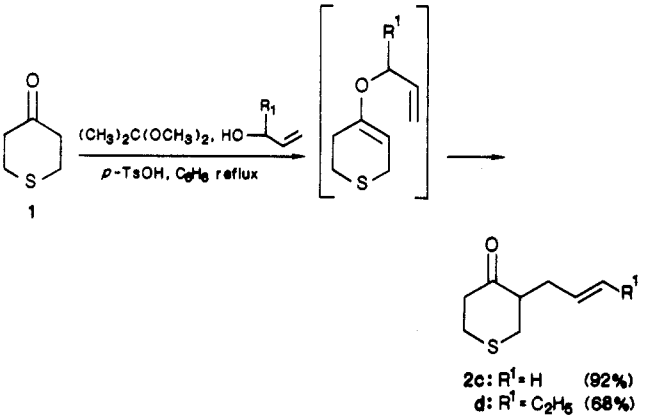
Scheme II[a]



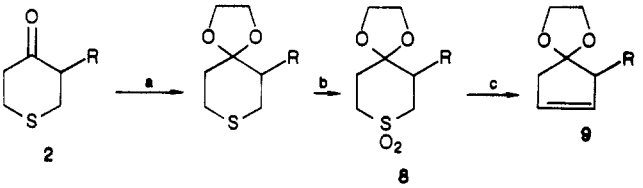
[a] (a) RX, K_2CO_3, acetone reflux; (b) RX, Me_2SO, 25 °C; (c) LiCl, HMPA, 80 °C, or NaCl, wet Me_2SO, 150 °C.

active functional group for a ring transformation. However, organic syntheses using 4-thianone have been little studied and only a few examples such as steroid synthesis by the use of *S*-methyl-4-oxothianium ion[2] and optically active alcohol synthesis by enzymic reduction of 4-thianone[3] have been reported. In recent years, there have been a few reports on the synthesis of 3-cyclopentenones,[4] although much work has been devoted to preparation of 2-cyclopentenones.[5] We have been interested in the synthesis of fragrant compounds such as methyl jasmonate and methyl dihydrojasmonate and also in search of new synthetic fragrant compounds. Therefore we have examined the ring transformation of 4-thianone to cyclopentenone by the use of Ramberg–Bäcklund-type reactions. The Ramberg–Bäcklund reaction represented one of the first alkene syntheses in which the position of double

Scheme III



Scheme IV[a]



[a] (a) $HOCH_2CH_2OH$, *p*-TsOH, C_6H_6 reflux, 5 h; (b) $NaIO_4$, CH_3OH–H_2O, 60 °C, 5 h; (c) *t*-BuOK, CCl_4, *t*-BuOH, 50 °C, 20 h.

Table I. Cyclopentene 9 Obtained by the One-Pot Ramberg–Bäcklund Reaction of 8

	cyclopentene 9		
sulfone 8		R	yield of 9, %
8a	9a	$C_6H_5CH_2$	84
8b	9b	*n*-C_5H_{11}	50
8c	9c	CH_2=$CHCH_2$	73
8d	9d	C_2H_5CH=$CHCH_2$	77
8e[a]	9e	*n*-C_3H_7	60

[a] 8e was prepared by hydrogenation (H_2/Pt) of 8c.

bond is clearly defined.[6] So, 3-cyclopentenones can be prepared by the selective alkylation of 4-thianone (1), following the Ramberg–Bäcklund type reaction and acid-catalyzed cleavage of 1,3-dioxolane ring (Scheme I).

We now report details of our attempts to extend the scope of this new approach to 3-cyclopentenones.[7]

Results and Discussion

Preparation of 3-Alkyl-4-thianones. One route to 2-alkyl-3-cyclopentenones (4) starts from 3-alkyl-4-thianones (2). Starting materials, 3-alkyl-4-thianones (2), were prepared by two procedures: (a) alkylation of 3-(methoxycarbonyl)-4-thianone (6) with alkyl halides (RX, K_2CO_3, acetone reflux,[8] or potassium enolate isolated, RX, dimethyl sulfoxide (Me_2SO), 25 °C[9]), followed by demethoxycarbonylation of 7 (LiCl, hexamethylphosphoric triamide (HMPA), 80 °C)[10] (Scheme II), and (b) allylation

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(3) Takemura, T.; Jones, J. B. *J. Org. Chem.* **1983**, *48*, 791 and references cited therein.
(4) Typical procedures for the synthesis of 3-cyclopentenones. (a) Cyclization of *cis*-1,4-dichloro-2-butene with methyl (methylthio)methyl sulfoxide: Ogura, K.; Yamashita, M.; Suzuki, M.; Furukawa, S.; Tsuchihashi, G. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1637. (b) Pd(0)-catalyzed reaction of 1,3-diene epoxides: Suzuki, M.; Oda, Y.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 1623. (c) Jones oxidation of cyclopentenols; Grieco, P. A. *J. Org. Chem.* **1972**, *37*, 2363. (d) Thermolysis of vinyl cyclopropanes: Corey, E. J.; Walinsky, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 8932. Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* (*N.Y.*) **1985**, *33*, 247.
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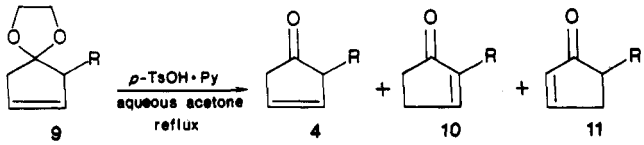
(8) Barco, A.; Benetti, S.; Pollini, G. P. *Synthesis*, **1973**, 316.
(9) 3-Alkyl-4-thianones (R = CH_3, C_2H_5): see ref 3. 2,3-Dialkylated 4-thianones: Lane, S.; Quick, S. J.; Taylor, R. J. K. *J. Chem. Soc., Perkin Trans. 1*, **1985**, 893.
(10) Müller, P.; Siegfried, B. *Tetrahedron Lett.* **1973**, 3565.

Table II. 3-Cyclopentenone 4 Obtained by Acid-Catalyzed Cleavage of the 1,3-Dioxolane Ring of 9

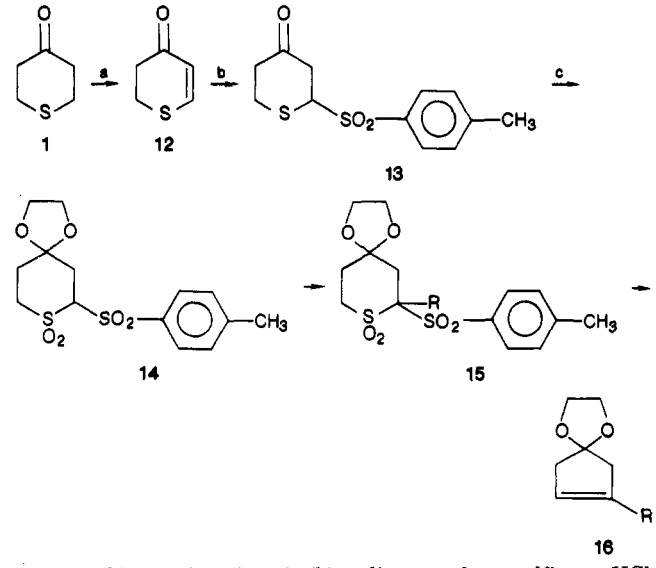


9 4 10 11

cyclopentene 9	R	cyclopentenone isomer ratio[a] 4:(10 + 11)	isolated yield of 4, %
9a	$C_6H_5CH_2$	91:9	53
9b	n-C_5H_{11}	94:6	78
9c	CH_2=$CHCH_2$	97:3	84
9d	C_2H_5CH=$CHCH_2$	88:12	79
9e	n-C_3H_7	91:9	70

[a] Determined by GC before purification of 4.

Scheme V[a]



1 12 13 14 15 16

[a] (a) NCS, pyridine (83%); (b) sodium p-toluenesulfinate, HCl, ethanol (94%); (c) $HOCH_2CH_2OH$, p-TsOH, C_6H_6, and then m-CPBA (92%).

by Claisen rearrangement of allyl vinyl ether[11] (Scheme III).

Synthesis of 2-Alkyl-3-cyclopentenones. 3-Alkyl-4-thianones **2** were quantitatively converted into 6-alkyl-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-dioxides (**8**) by protection of carbonyl group (ethylene glycol, p-toluenesulfonic acid (p-TsOH), benzene reflux), followed by oxidation ($NaIO_4$ (3 equiv), methanol–water, 60 °C). Six-membered sulfones **8** were transformed into cyclopentenes **9** by the Ramberg–Bäcklund reaction (t-BuOK, CCl_4, t-BuOH, 50 °C) under nitrogen in moderate yields (Scheme IV and Table I). After acid-catalyzed cleavage of the 1,3-dioxolane group in **9** (pyridinium p-toluenesulfonate (p-TsOH·Py) (catalyst), aqueous acetone reflux),[12] 3-cyclopentenones **4** were obtained as major components (>90%) with minor amounts of 2- and 4-cyclopentenone isomers. Pure 3-cyclopentenones **4** were isolated by column chromatography (Table II).

Synthesis of 3-Alkyl-3-cyclopentenones. Hitherto, there are two reports concerning the synthesis of 2-alkyl-4-thianones (**3**). One method is the reaction between

Table III. Reaction Conditions and Yields in the Conversion of 14 to 15

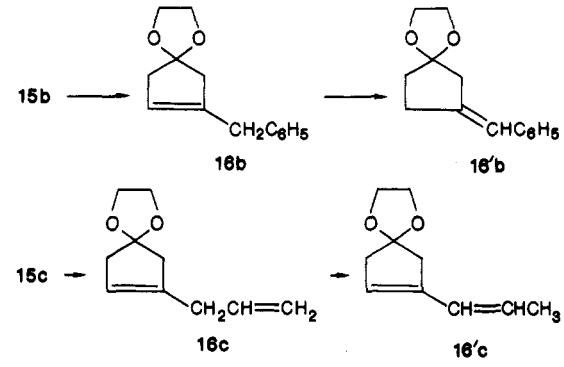
alkyl halides	method[a]	product	yield of 15, %
CH_3I	A	**15a**	96
$C_6H_5CH_2Br$	A	**15b**	88
CH_2=$CHCH_2Br$	A	**15c**	97
n-$C_5H_{11}I$	B	**15d**	86
$CH_3O(CO)(CH_2)_4CH_2I$	B	**15e**	93
$C_6H_5CH_2CH_2Br$	B	**15f**	80

[a] Method A: sulfone **14** (2 mmol), alkyl halide (4 mmol), K_2CO_3 (6 mmol), dry acetone (40 mL), reflux 6–10 h. Method B: sulfone **14** (2 mmol), alkyl halide (4 mmol), NaH (2.5 mmol), dry DMF (20 mL), 70 °C, 20–24 h.

Table IV. Cyclopentene 16 Obtained by the Ramberg–Bäcklund-Type Reaction of 15

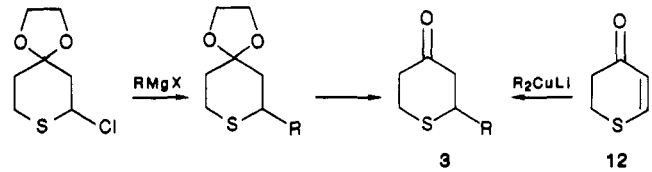
sulfone 15	cyclopentene 16	R	yield of 16, %
15a	**16a**	CH_3	60
15d	**16d**	n-C_5H_{11}	87
15f	**16f**	$C_6H_5CH_2CH_2$	70

Scheme VI



15b 16b 16'b 15c 16c 16'c

Grignard reagents and 2-chlorothiane derivative.[13] Another method starts with organocopper reagents and 2,3-dihydrothiin-4-one.[14] Our synthetic plan utilizes a new



3 12

type of leaving group such as the toluenesulfinate ion instead of a halogen ion under Ramberg–Bäcklund-type reaction conditions. Target compound **14** can stabilize a carbanion at the α-position of a sulfone and give regioselective alkylation. p-Toluenesulfinate ion also acts as a good leaving group in the presence of base such as sodium hydride in Me_2SO, and **15** can be transformed into cyclopentenes **16**. We found actually that α-alkyl-α-(p-tolylsulfonyl)thiane S,S-dioxides **15** were successfully converted into the corresponding cyclopentenes **16** by the action of NaH–KH in dimethyl sulfoxide (Me_2SO) in good yields. The key compound **14** was readily prepared according to Scheme V. 2,3-Dihydrothiin-4-one **12** was converted into 1,4-dioxa-7-(p-tolylsulfonyl)-8-thiaspiro[4.5]decane 8,8-dioxide (**14**) by 1,4-addition of p-toluenesulfinic acid (sodium p-toluenesulfinate, HCl, ethanol, 0 °C → room temperature), protection of carbonyl group of **13** (ethylene

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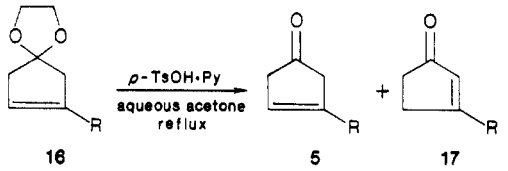
(14) Batten, R. J.; Coyle, J. D.; Taylor, R. J. K. *Synthesis*, **1980**, 910.

Table V. 3-Cyclopentenone 5 Obtained by Acid-Catalyzed Cleavage of the 1,3-Dioxolane Ring of 16



16 5 17

cyclopentene 16			yield of 5	isomer
	R	reacn time, h	+ 17, %	ratio[a] 5:17
16a	CH_3	10	50	100:0
16d	n-C_5H_{11}	10	94	82:18
		22	92	75:25
16f	$C_6H_5CH_2CH_2$	10	82	85:15

[a] Determined by GC.

glycol, *p*-toluenesulfonic acid (catalyst), benzene reflux), followed by oxidation (*m*-chloroperbenzoic acid (3 equiv), CH_2Cl_2, 0 °C → room temperature). For the regioselective alkylation of **14** with alkyl halides (RX), two types of procedure were employed: (a) with K_2CO_3 in dry acetone (reflux; method A) and (b) with NaH in *N,N*-dimethylformamide (DMF) (70 °C; method B). The results are summarized in Table III, showing that both method A and method B gave monoalkylated sulfone **15** in good yields. Sulfones **15** were transformed into cyclopentenes **16** by the Ramberg–Bäcklund reaction (NaH (2.5–3 equiv)–KH (0.1–1 equiv), Me_2SO, 20–30 °C, 24–48 h) under nitrogen (Table IV). In the case of **15b** (R = $C_6H_5CH_2$) and **15c** (R = CH_2=$CHCH_2$), benzylic or allylic proton was removed by base and isomerization of the resulting cyclopentene **16b** or **16c** was observed under these Ramberg–Bäcklund reaction conditions (even in the presence of only sodium hydride in Me_2SO at 40 °C) to give isomer **16'b** or **16'c** (Scheme VI). After acid-catalyzed cleavage of the 1,3-dioxolane group in **16**, (*p*-TsOH·pyridine (catalyst), aqueous acetone reflux), the expected 3-cyclopentenones **5** were formed as major component (>80%) along with minor amount of 2-cyclopentenone isomer **17** (by a GC analysis) (Table V). The ratio of 3-cyclopentenone/2-cyclopentenone decreased with increasing reaction time.

In conclusion, this synthetic approach from 4-thianone (**1**) to alkyl-substituted 3-cyclopentenones **4** and **5** offers several advantages: (i) The starting material **1** and reagents used are readily available; (ii) all operations in the reaction steps are simple; (iii) the yields are moderate to good. The yields of the various steps have not been optimized. Further development and applications of this method are in progress and will be reported later.

Experimental Section

Proton magnetic resonance spectra were recorded on a JEOL PMX 60SI 60-MHz spectrometer, and carbon-13 NMR spectra were recorded on a JEOL FX-60 spectrometer. Infrared spectra were recorded on a Hitachi 260-10 spectrometer. Mass spectra were determined with a JEOL JMX-DX 300 mass spectrometer with JEOL JMA 5000 mass data system at an ionizing voltage of 70 eV. Melting points (uncorrected) were determined on a Yamato MP-21 apparatus in open capillary tubes. GLPC were recorded on a Hitachi 163 with 10% Apiezon L 2-m column. A normal workup procedure consisted of three extractions with the specified solvent, washing combined extracts with water, drying ($MgSO_4$ or Na_2SO_4), and removal of the solvent on a rotary evaporator under reduced pressure. Dimethyl sulfoxide, DMF, *tert*-butyl alcohol, and carbon tetrachloride were dried over molecular sieves (3 Å) (Wako Chemicals). Column chromatography was performed with Wako gel C-200 or Florisil (Wako Chemicals). Thin-layer chromatography was performed on 0.25-mm silica gel, glass-backed plates (Merck $60F_{254}$). Elemental analyses were performed at the Department of Chemistry, Tokyo Metropolitan University. High-resolution mass spectra were performed with a JEOL JMX-DX 300 mass spectrometer (resolution 5000).

3-(Methoxycarbonyl)-4-thianone (6). Dimethyl 3,3'-thiodipropanoate was obtained by esterification of the dicarboxylic acid[2] in methanol in the presence of concentrated H_2SO_4. This diester was then converted into 3-(methoxycarbonyl)-4-thianone (**6**) in 71% yield as described by Fehnel and Carmack;[15] bp 97.5–100 °C (2 mmHg) [lit.[15] bp 120–125 °C (5 mmHg)]: mp 67.7–69.0 °C (hexane); IR (neat) 1745 (ester C=O), 1715 (keto C=O), 1660 (enolic C=O), 1615 cm^{-1} (enolic C=C); IR (KBr) 1725 (ester C=O), 1710 cm^{-1} (keto C=O); ^1H NMR ($CDCl_3$) δ 2.20–2.90 (m, 4 H), 3.19 (br s, 2 H), 3.63 (s, 3 H), 12.30 (s, 1 H, enolic proton).

4-Thianone (1). In a 300-mL flask fitted with reflux condenser was placed 3-(methoxycarbonyl)-4-thianone (**6**) (82.6 g, 0.475 mol) with 5% sulfuric acid (200 mL). The above mixture was refluxed with vigorous stirring for 5 h. After the solution was cooled, the product was extracted with dichloromethane (100 mL × 2), and the organic layer was washed with 10% sodium carbonate (50 mL × 2) and water (50 mL × 2) and dried over magnesium sulfate. Removal of the solvent gave a white solid: yield, 50.0 g (91%); mp 59.2–61.0 °C (hexane–dichloromethane) [lit.[2] mp 60 °C]; IR (KBr) 1705 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.35–2.40 (m, 4 H), 2.47–2.92 (m, 4 H); MS, *m/z* 116 ($M^{+\cdot}$).

General Procedure for Alkylation of 4-Thianone: 3-Benzyl-4-thianone (2a). An acetone solution (40 mL) of 3-(methoxycarbonyl)-4-thianone (**6**) (1.70 g, 10 mmol), benzyl bromide (2.00 g, 12.0 mmol), and potassium carbonate (4.20 g, 30.0 mmol) was stirred for 20 h under acetone reflux conditions. After the acetone was removed under vacuum, water was added to the residue, and the product was extracted with ether. The ether extract was washed with brine and dried over magnesium sulfate. Pure product **7a** was obtained by silica gel column chromatography (hexane/ether, 4/1): 2.17 g (82%); mp 64.5–65.3 °C (hexane); IR (KBr) 1750, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.71 (br s, 5 H), 2.97–3.30 (m containing d at 3.04 (J = 6.6 Hz, 3 H), 3.49 (s, 3 H), 7.05 (br s, 5 H); ^{13}C NMR ($CDCl_3$) δ 30.6, 37.9, 39.7, 43.4, 52.3, 64.2 (OCH_3), 126.9, 128.1, 130.4, 135.6, 170.5 (ester C=O), 204.7 (keto C=O); MS, *m/z* 264.0786 (calcd for $C_{14}H_{16}O_3S$, 264.0820).

A mixture of 3-benzyl-3-(methoxycarbonyl)-4-thianone (**7a**) (1.10 g, 4 mmol), sodium chloride (0.26 g, 4.40 mmol), and water (0.22 g, 12.0 mmol) in Me_2SO (5 mL) was heated (oil bath temperature, 150 °C) for 20 h. After the solution was cooled to room temperature, the product was extracted with ether, and the ether extracts were washed with water and brine and dried over magnesium sulfate. Chromatography (on silica gel) and vacuum distillation gave 3-benzyl-4-thianone (**2a**) as a colorless oil (0.49 g, 60%): bp 149 °C (2 mmHg); IR (neat) 1705 (C=O) and 1490 cm^{-1} (aryl); ^1H NMR ($CDCl_3$) δ 2.40–3.30 (m, 9 H), 7.10 (br s, 5 H); ^{13}C NMR ($CDCl_3$) δ 30.8, 35.0, 35.2, 43.9, 54.5, 126.3, 128.4, 129.0, 130.8, 205.5 (C=O); MS, *m/z* 206.0787 (calcd for $C_{12}H_{14}OS$, 206.0766).

3-*n*-Pentyl-3-(methoxycarbonyl)-4-thianone (7b). To an aqueous methanol solution (water, 2.6 mL; methanol, 25 mL) of potassium hydroxide (4.40 g, 66.7 mmol) was added 3-(methoxycarbonyl)-4-thianone (**6**) (11.6 g, 66.7 mmol) with stirring under ice–water cooling conditions. After the white solids were separated, methanol (2 mL) and ether (12 mL) were added to the above mixture, and the mixture was stirred. The solids were filtered and washed with cold methanol (15 mL) and ether (15 mL) and dried under vacuum: yield, 11.5 g (81%). The above potassium salt of enolate (6.00 g, 28.0 mmol) was dissolved in dry Me_2SO (50 mL), and 1-iodopentane (11.1 g, 56.0 mmol) was added to it during 20 min under N_2 atmosphere. The mixture was stirred for another 20 h at room temperature. The reaction solution was poured into water, and the product was extracted with chloroform

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(50 mL × 3). The chloroform extracts were washed successively with water (50 mL × 3), 10% sodium thiosulfate (50 mL × 3), water (50 mL × 3), and dried over magnesium sulfate. After removal of solvent, 3-*n*-pentyl-3-(methoxycarbonyl)-4-thianone (**7b**) was purified by distillation: yield, 4.89 g (72%); bp 138 °C (2.5 mmHg); IR (neat) 1735 (ester C=O), 1710 cm^{-1} (keto C=O); ^1H NMR ($CDCl_3$) δ 0.97 (t, 3 H), 1.00–1.50 (m, 8 H), 2.84–3.46 (m, 6 H), 3.77 (s, 3 H); MS, *m/z* 244.1217 (calcd for $C_{12}H_{20}O_3S$, 244.1133).

3-*n*-Pentyl-4-thianone (2b). A mixture of 3-*n*-pentyl-3-(methoxycarbonyl)-4-thianone (**7b**) (2.60 g, 9.8 mmol) and lithium chloride (0.85 g, 18.6 mmol) in dry HMPA (20 mL) was stirred at 65–75 °C for 20 h. After the reaction mixture was cooled, the product was extracted with ether (100 mL), and the ether extract was washed with water (50 mL × 5) and brine (30 mL) and dried over magnesium sulfate. Silica gel column chromatography gave **2b** as an oil (hexane/ether, 4/1): yield, 1.30 g (65%); IR (neat) 1705 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.90 (br t, 3 H), 1.29–1.33 (m, 8 H), 2.60–3.10 (m, 7 H); MS, *m/z* 186.1063 (calcd for $C_{10}H_{18}OS$, 186.1078).

Allylation of 4-Thianone via Claisen Rearrangement: 3-Allyl-4-thianone (2c). A benzene solution (15 mL) of 4-thianone (1) (3.00 g, 26.0 mmol), allyl alcohol (3.30 g, 57.0 mmol), 2,2-dimethoxypropane (3.31 g, 31.2 mmol), and *p*-toluenesulfonic acid (20 mg, catalytic) was heated; acetone, methanol, and benzene were slowly distilled away during 6 h. Then, most of the solvent was distilled, toluene (80 mL) was added to the residual solution, and allyl alcohol–toluene mixture was distilled away as an azeotropic mixture. After removal of toluene under vacuum, the product was purified by silica gel column chromatography (hexane/ether, 4/1), followed by distillation: 3.37 g (92%); bp 78.8–80.0 °C (1.5 mmHg); IR (neat) 3075, 1710 (C=O), 1640 (C=C), 920 cm^{-1} (C=CH_2); ^1H NMR ($CDCl_3$) δ 1.55–2.20 (m, 9 H), 3.88 (s, 4 H), 4.70–5.13 (m, 2 H), 5.30–6.00 (m, 1 H); MS, *m/z* 156.0597 (calcd for $C_8H_{12}OS$, 156.0608).

3-[(*E*)-2-Pentenyl]-4-thianone (2d). Following the general procedure described above for the synthesis of 3-allyl-4-thianone (**2c**), 4-thianone (1) was alkylated (4-thianone (10.0 g, 86.2 mmol), 1-penten-3-ol (18.9 g, 220 mmol), 2,2-dimethoxypropane (12.5 g, 120 mmol), *p*-toluenesulfonic acid (60 mg), benzene (50 mL), and then toluene (200 mL)). Silica gel column chromatography (hexane/ether, 7/2) gave 3-[(*E*)-2-pentenyl]-4-thianone (**2d**) (10.80 g, 68% yield) and unreacted 4-thianone (1) (2.50 g). **2d** was further purified by distillation: bp 110–120 °C (5 mmHg); IR (neat) 1715 (C=O), 970 cm^{-1} (trans —CH=CH—); ^1H NMR ($CDCl_3$) δ 0.97 (t, *J* = 7.2 Hz, 3 H), 1.92–2.36 (m, 4 H), 2.48–3.20 (m, 7 H), 5.24–5.86 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.77, 25.52, 30.78, 32.34, 35.06, 43.83, 52.72, 125.19, 135.06, 209.46; MS, *m/z* 184.0897 (calcd for $C_{10}H_{16}OS$, 184.0922).

6-Benzyl-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-Dioxide (8a). A benzene solution (50 mL) of 3-benzyl-4-thianone (**2a**) (1.10 g, 5.34 mmol), ethylene glycol (0.64 g, 10.7 mmol), and *p*-toluenesulfonic acid (20 mg) was refluxed for 4 h with azeotropic removal of water by the apparatus fitted with Dean–Stark condenser. After the above reaction mixture was cooled, the benzene solution was washed with 5% sodium bicarbonate (30 mL) and water (30 mL) and dried over sodium sulfate to give the ketal: IR (neat) 1490 cm^{-1} (aryl); ^1H NMR ($CDCl_3$) δ 1.72–3.00 (m, 9 H), 3.87 (s, 4 H), 7.12 (br s, 5 H).

The ketal obtained was used for next step without further purification. The ketal was oxidized with sodium periodate (2.85 g, 13.3 mmol) at room temperature for 30 min and then at 60 °C for 10 h in aqueous methanol (water/methanol, 4/5; 40 mL) with vigorous stirring. After the reaction mixture was cooled, methanol was removed under vacuum. To the above residue was added chloroform (50 mL), and the mixture was stirred and filtered to remove sodium iodate. The solids were washed with chloroform (50 mL), and the combined chloroform extracts were dried over sodium sulfate. After removal of the solvent, a white solid was obtained and recrystallized from ethanol: yield, 1.21 g (81%); mp 175.5–176.5 °C (95% ethanol); IR (KBr) 1490 (aryl), 1290, 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.05–3.50 (m, 9 H), 4.07 (s, 4 H), 7.05–7.30 (m, 5 H); MS, *m/z* 282 ($M^{\cdot+}$). Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.57; H, 6.38. Found: C, 59.67; H, 6.37.

6-Allyl-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-Dioxide (8c). Following the general procedure described above for the preparation of **8a**, 3-allyl-4-thianone (**2c**) (14.0 g, 89.7 mmol) was transformed into the ketal (ethylene glycol (6.48 g, 108 mmol), *p*-toluenesulfonic acid (40 mg), and benzene (120 mL)): IR (neat) 3075, 1640 (C=C), 920 cm^{-1} (CH=CH_2); ^1H NMR ($CDCl_3$) δ 1.55–2.70 (m, 9 H), 3.88 (s, 4 H), 4.70–5.13 (m, 2 H), 5.30–6.00 (m, 1 H).

The ketal was oxidized to the sulfone with sodium periodate (50.0 g, 23.4 mmol) in aqueous methanol (500 mL): yield, 19.4 g (92%); mp 100.3–102.3 °C (methanol/hexane); IR (KBr) 3080, 1640 (C=C), 1290, 1120 (SO_2), 925 cm^{-1} (CH=CH_2); ^1H NMR ($CDCl_3$) δ 1.70–3.20 (m, 9 H), 3.99 (s, 4 H), 4.75–6.04 (m, 3 H); MS, *m/z* 233 ($M^{\cdot+}$ + 1). Anal. Calcd for $C_{10}H_{16}O_4S$: C, 51.72; H, 6.90. Found: C, 51.78; H, 6.86.

6-[(*E*)-2-Pentenyl]-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-Dioxide (8d). Following the general procedure described above for the preparation of **8a**, 3-[(*E*)-2-pentenyl]-4-thianone (**2d**) (10.0 g, 54.3 mmol) was transformed into the ketal (ethylene glycol (6.5 g, 109 mmol), *p*-toluenesulfonic acid (30 mg), and benzene (60 mL)): IR (neat) 970 cm^{-1} (trans —CH=CH—); ^1H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.2 Hz, 3 H), 1.26–2.25 (m containing s at 1.27, 11 H), 5.17–5.38 (m, 2 H); MS, *m/z* 228 ($M^{\cdot+}$).

The ketal was oxidized to sulfone with sodium periodate (34.9 g, 163 mmol) in aqueous methanol (water/methanol, 2/3; 300 mL): yield, 12.63 g (90%); mp 109.5–110.0 °C (methanol); IR (KBr) 1290, 1135 (SO_2), 970 cm^{-1} (trans —CH=CH—); ^1H NMR ($CDCl_3$) δ 0.93 (t, *J* = 6.6 Hz, 3 H), 1.54–2.55 (m, 7 H), 2.80–3.05 (m, 4 H), 3.85 (s, 4 H), 5.00–5.41 (m, 2 H); MS, *m/z* 260 ($M^{\cdot+}$). Anal. Calcd for $C_{14}H_{20}O_4S$: C, 55.36; H, 7.74. Found: C, 55.61; H, 7.91.

6-*n*-Propyl-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-Dioxide (8e). Compound **8e** was obtained by the hydrogenation of **8c** (1.15 g, 4.96 mmol) in the presence of platinum oxide (22.5 mg, 0.10 mmol) in ethanol (40 mL): yield, 1.08 g (93%); mp 105.5–106.5 °C (methanol/hexane); IR (KBr) 1285, 1105 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 0.63–1.60 (m, 7 H), 2.00–2.65 (m, 3 H), 2.94–3.25 (m, 4 H), 3.97 (s, 4 H); MS, *m/z* 234 ($M^{\cdot+}$). Anal. Calcd for $C_{10}H_{18}O_4S$: C, 51.26; H, 7.74. Found: C, 51.13; H, 7.86.

6-*n*-Pentyl-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-Dioxide (8b). Compound **8b** was prepared by hydrogenation of **8d** (0.81 g, 3.10 mmol) in ethanol (40 mL) in the presence of platinum oxide (20.0 mg, 0.08 mmol): yield, 0.816 g (100%); mp 92.5–93.6 °C (methanol/hexane); IR (KBr) 1280, 1135 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 0.70–1.60 (m, 11 H), 1.80–2.39 (m, 3 H), 2.88–3.34 (m, 4 H), 3.98 (s, 4 H); MS, *m/z* 263 ($M^{\cdot+}$ + 1). Anal. Calcd for $C_{12}H_{22}O_4S$: C, 54.94; H, 8.45. Found: C, 54.68; H, 8.37.

6-Benzyl-1,4-dioxaspiro[4.4]non-7-ene (9a). 6-Benzyl-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-dioxide (**8a**) (0.230 g, 0.82 mmol) was dissolved in carbon tetrachloride (20 mL) and dry *tert*-butyl alcohol (10 mL), and to the above solution was added potassium *tert*-butoxide (2.00 g, 16.4 mmol) below 50 °C under N_2 atmosphere. The mixture was stirred for 20 h at 50–55 °C. After reaction, the solution was cooled to room temperature, the solution was poured into water (30 mL), and the product was extracted with ether (30 mL × 3). The ether extract was washed with water (30 mL × 3) and brine (30 mL) and dried over sodium sulfate. After removal of the solvent, the product was purified by Florisil column chromatography (hexane/ether, 4/1): yield 0.143 g (84%); IR (neat) 3050, 3020, 1490 (aryl), 700 cm^{-1} (—CH=CH—); ^1H NMR ($CDCl_3$) δ 2.30–3.00 (m, 5 H), 3.79 (d, *J* = 1.2 Hz, 4 H), 5.60 (m, 2 H), 7.18 (s, 5 H); MS, 216.1140 (calcd for $C_{14}H_{16}O_2$, 216.1150).

6-*n*-Pentyl-1,4-dioxaspiro[4.4]non-7-ene (9b). Following the general procedure described above for the preparation of **9a**, **8b** (0.524 g, 2.0 mmol) was transformed into cyclopentene **9b** (potassium *tert*-butoxide (2.44 g, 20.0 mmol), carbon tetrachloride (20 mL), and *tert*-butyl alcohol (10 mL)): yield, 0.196 g (50%); IR (neat) 3050, 700 cm^{-1} (—CH=CH—); ^1H NMR ($CDCl_3$) δ 0.60–1.74 (m, 11 H), 2.27–2.80 (m, 3 H), 3.89 (s, 4 H), 5.63–5.78 (m, 2 H); MS, *m/z* 196.1483 (calcd for $C_{12}H_{20}O_2$, 196.1463).

6-Allyl-1,4-dioxaspiro[4.4]non-7-ene (9c). Following the general procedure described above for the preparation of **9a**, **8c** (0.464 g, 2.0 mmol) was transformed into cyclopentene (potassium *tert*-butoxide (2.44 g, 20.0 mmol), carbon tetrachloride (20 mL), and *tert*-butyl alcohol (10 mL)): yield, 0.240 g (73%); IR (neat) 3060, 1640 (C=C), 910 (—CH=CH_2), 700 cm^{-1} (—CH=CH—); ^1H NMR ($CDCl_3$) δ 1.75–2.75 (m, 5 H), 3.76 (s, 4 H), 4.65–5.08

(m, 2 H), 5.34–6.09 (m containing s at 5.56, 3 H); MS, m/z 166.0984 (calcd for $C_{10}H_{14}O_2$, 166.0994).

6-[(*E*)-2-Pentenyl]-1,4-dioxaspiro[4.4]non-7-ene (9d). Following the general procedure described above for the preparation of **9a**, **8d** (0.520 g, 2.0 mmol) was transformed into cyclopentene **9d** (potassium *tert*-butoxide (2.44 g, 20.0 mmol), carbon tetrachloride (20 mL), and *tert*-butyl alcohol (10 mL)): yield, 0.300 g (77%); IR (neat) 3050, 3020, 970 (trans —CH=CH—), 700 cm^{-1} (—CH=CH—); ^1H NMR ($CDCl_3$) δ 0.96 (t, J = 7.2 Hz, 3 H), 2.66–2.90 (m containing br s at 2.50, 7 H), 3.87 (s, 4 H), 5.30–5.47 (m, 2 H), 5.58 (s, 2 H); MS, m/z 194.1338 (calcd for $C_{12}H_{18}O_2$, 194.1307).

6-*n*-Propyl-1,4-dioxaspiro[4.4]non-7-ene (9e). Following the general procedure described above for the preparation of **9a**, **8e** (0.470 g, 2.0 mmol) was transformed into cyclopentene **9e** (potassium *tert*-butoxide (2.44 g, 20.0 mmol), carbon tetrachloride (20 mL), and *tert*-butyl alcohol (10 mL)): yield, 0.202 g (60%); IR (neat) 3060, 700 cm^{-1} (—CH=CH—); ^1H NMR ($CDCl_3$) δ 0.56–1.57 (m, 7 H), 2.18–2.70 (m, 3 H), 3.84 (s, 4 H), 5.63 (s, 2 H); MS, m/z 168.1142 (calcd for $C_{10}H_{16}O_2$, 168.1150).

2-Benzyl-3-cyclopentenone (4a). An acetone solution (20% aqueous; 20 mL) of 6-benzyl-1,4-dioxaspiro[4.4]non-7-ene (**9a**) (0.200 g, 1.16 mmol) and pyridinium *p*-toluenesulfonate (30 mg, 0.1 equiv) was refluxed for 21–24 h. After the solution was cooled, the reaction solution was checked by GLPC (Apiezon L, 10%, 2-m column), and the isomer ratio of 3-cyclopentenone (**4a**) and 2- and/or 4-cyclopentenone isomers (**10** and/or **11**) (**4a**/(**10** + **11**) = 91:9) was determined. After removal of acetone, the products were extracted with ether (50 mL). After normal workup, Florisil column chromatography (hexane/ether, 4/1) gave the 3-cyclopentenone **4a** as an oil: yield, 0.106 g (53%); IR (neat) 3050, 3020, 1745 (C=O), 1600, 1495 (aryl), 700 cm^{-1} (—CH=CH—); ^1H NMR ($CDCl_3$) δ 2.20–3.14 (m, 5 H), 5.82 (s, 2 H), 7.02 (s, 5 H); MS, m/z 172.0868 (calcd for $C_{12}H_{12}O$, 172.0888).

2-*n*-Pentyl-3-cyclopentenone (4b). Acid-catalyzed cleavage of the 1,3-dioxolane ring of **9b** (0.150 g, 0.77 mmol) with pyridinium *p*-toluenesulfonate (20 mg, 0.1 equiv) in 20% aqueous acetone (30 mL) gave **4b** and **10b** and/or **11b** (3-cyclopentenone (**4b**)/2- and 4-cyclopentenone isomers (**10b** + **11b**) = 94:6, checked by GLPC, Apiezon L, 10%, 2-m column, 120 °C): yield, 91.0 mg (78%); IR (neat) 3055, 1745 (C=O), 700 cm^{-1} (—CH=CH—); ^1H NMR ($CDCl_3$) δ 0.61–1.70 (m, 11 H), 2.57–3.08 (m, 3 H), 6.07 (s, 2 H); MS, m/z 152.1190 (calcd for $C_{10}H_{16}O$, 152.1201).

2-Allyl-3-cyclopentenone (4c). Acid-catalyzed cleavage of the 1,3-dioxolane ring of **9c** (0.270 g, 1.60 mmol) with pyridinium *p*-toluenesulfonate (30 mg, 0.1 equiv) in 20% aqueous acetone (30 mL) gave **4c** and **10c** and/or **11c** (3-cyclopentenone (**4c**)/2- and 4-cyclopentenone (**10c** + **11c**) = 97:3, by GLPC, Apiezone L, 10%, 2-m column, 110 °C). **4c** was purified by column chromatography: yield, 0.163 g (84%); IR (neat) 3070, 1745 (C=O), 1640 (C=C), 915 (—CH=CH_2), 700 cm^{-1} (—CH=CH—); ^1H NMR ($CDCl_3$) δ 1.95–3.10 (m containing s at 2.74, 5 H), 4.78–5.26 (m, 2 H), 5.51–6.23 (m containing s at 6.06, 3 H); MS, m/z 122.0712 (calcd for $C_8H_{10}O$, 122.0732).

2-[(*E*)-2-Pentenyl]-3-cyclopentenone (4d). Acid-catalyzed cleavage of **9d** (0.150 g, 0.773 mmol) with pyridinium *p*-toluenesulfonate (20 mg, 0.1 equiv) in 20% aqueous acetone (20 mL) gave 3-cyclopentenone **4d** and **10d** and/or **11d** (**4d**/(**10d** + **11d**) = 88:12, checked by GLPC, Apiezone L, 10%, 2-m column, 120 °C). **4d** was purified by column chromatography: yield, 82.0 mg (79%); IR (neat) 3075, 3040, 1740 (C=O), 970 (trans —CH=CH—), 700 cm^{-1} (—CH=CH—); ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.2 Hz, 3 H), 1.70–2.97 (m containing s at 2.80, 7 H), 5.34–5.55 (m, 2 H), 6.05 (s, 2 H); MS, m/z 150.1085 (calcd for $C_{10}H_{14}O$, 150.1085).

2-*n*-Propyl-3-cyclopentenone (4e). Acid-catalyzed cleavage of the 1,3-dioxolane ring of **9e** (60.0 mg, 0.36 mmol) with pyridinium *p*-toluenesulfonate (10 mg, 0.1 equiv) in 20% aqueous acetone (20 mL) gave **4e** and **10e** and/or **11e** (**4e**/(**10e** + **11e**) = 91:9, checked by GLPC, Apiezone L, 10%, 2-m column, 100 °C). **4e** was purified by column chromatography: yield, 31.8 mg (70%); IR (neat) 3060, 1745 (C=O), 700 cm^{-1} (—CH=CH—); ^1H NMR ($CDCl_3$) δ 0.65–1.70 (m, 7 H), 2.35–2.88 (m, 3 H), 6.07 (s, 2 H); MS, m/z 124.0890 (calcd for $C_8H_{12}O$, 124.0888).

2-(*p*-Tolylsulfonyl)-4-thianone (13). Concentrated HCl (12 N, 1.67 mL, 20 mmol) was added to a magnetically stirred solution of sodium *p*-toluenesulfinate·$4H_2O$ (5.0 g, 20 mmol) in 99% ethanol (50 mL) at 0 °C with an ice cooling bath. After the addition was completed, stirring was continued at 0 °C for 10 min. 2,3-Dihydrothiin-4-one (**12**)[14] (2.28 g, 20 mmol) in 99% ethanol (10 mL) was then added to the above solution. The solution was stirred for 5 h at room temperature. After removal of ethanol under vacuum, water (30 mL) and chloroform (100 mL) were added to the residue. The chloroform layer was washed with brine and dried over magnesium sulfate, and the solvent was removed under vacuum. The crude product was recrystallized from ethanol, yielding 5.05 g (94%): mp 113.0 °C dec; ^1H NMR ($CDCl_3$) δ 2.47 (s, 3 H), 2.70–3.10 (m, 5 H), 3.20–4.00 (m, 1 H), 4.34 (br t, J = 5 Hz, 1 H), 7.33 and 7.77 (A_2B_2 m, J = 8 Hz, 4 H); IR (KBr) 1710 (C=O), 1310, 1140 cm^{-1} (SO_2); MS, m/z 270 ($M^{\cdot+}$). Anal. Calcd for $C_{12}H_{14}O_3S_2$: C, 53.31; H, 5.22. Found: C, 53.46; H, 5.26.

7-(*p*-Tolylsulfonyl)-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-Dioxide (14). 2-(*p*-Tolylsulfonyl)-4-thianone (**13**) (0.88 g, 3.29 mmol) was dissolved in 30 mL of benzene with ethylene glycol (0.306 g, 4.94 mmol) and a catalytic amount of *p*-toluenesulfonic acid (20 mg) in a 50-mL round-bottomed flask fitted with a Dean–Stark trap. The ketone was ketalized by heating to reflux for 4 h and removing water by azeotropic distillation. The reaction mixture was cooled to room temperature, the benzene was removed under vacuum, and the residue was dissolved in 30 mL of dichloromethane. *m*-Chloroperbenzoic acid (1.70 g, 9.87 mmol) was added over 5 min to the magnetically stirred above solution at 0 °C. The solution was stirred at 0 °C for 1 h and then at room temperature for 4 h. Water (10 mL) was added to the above mixture, and the resulting mixture was washed with 10% potassium carbonate solution (30 mL × 5) and brine. The organic layer was dried over sodium sulfate and evaporated under vacuum to afford 1.04 g (92%) of a solid: mp 216.5–218.2 °C dec (ethanol/chloroform); ^1H NMR ($CDCl_3$) δ 2.00–2.70 (m containing s at 2.47, 7 H), 3.00–3.40 (m, 2 H), 4.03 (s, 4 H), 4.57 (dd, J = 10 and 6 Hz, 1 H), 7.37 and 7.88 (A_2B_2 m, J = 8 Hz, 4 H); IR (KBr) 1335, 1300 (SO_2 asymmetrical and 1145, 1110 cm^{-1} (SO_2 symmetrical); MS, m/z 346 ($M^{\cdot+}$). Anal. Calcd for $C_{14}H_{18}O_6S_2$: C, 48.54; H, 5.24. Found: C, 48.24; H, 5.18.

7-Methyl-7-(*p*-tolylsulfonyl)-1,4-dioxa-8-thiaspiro[4.5]-decane 8,8-Dioxide (15a). 2-(*p*-Tolylsulfonyl)-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-dioxide (**14**) (0.614 g, 1.77 mmol) and 0.735 g (5.32 mmol) of anhydrous potassium carbonate were combined in 40 mL of dry acetone and heated to reflux for 1 h. Acetone solution (10 mL) of methyl iodide (0.503 g, 3.54 mmol) was added dropwise with stirring to the above solution. After 5 h of refluxing, acetone was evaporated under vacuum to dryness, and the resulting residue was extracted with chloroform (50 mL). The chloroform solution was washed with water (30 mL × 2) and dried over sodium sulfate, and the solvent was removed under vacuum. The crude product was recrystallized from ethanol, yielding 0.609 g (96%); mp 175.0–175.5 °C dec; ^1H NMR ($CDCl_3$) δ 1.82 (s, 3 H), 1.92–3.43 (m containing s at 2.43, 9 H), 3.95 (s, 4 H), 7.22 and 7.78 (A_2B_2 m, J = 9 Hz, 4 H): IR (KBr) 1330, 1305 (SO_2 asymmetrical), 1150, 1105 cm^{-1} (SO_2 symmetrical); MS, m/z 386 ($M^{\cdot+}$). Anal. Calcd for $C_{15}H_{20}O_6S_2$: C, 49.98; H, 5.59. Found: 50.36; H, 5.70.

7-Benzyl-7-(*p*-tolylsulfonyl)-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-Dioxide (15b). An acetone solution (40 mL) of **14** (1.73 g, 5.0 mmol), benzyl bromide (1.71 g, 10.0 mmol), and potassium carbonate (2.07 g, 15.0 mmol) was stirred for 24 h under acetone reflux conditions. After acetone was removed under vacuum, water was added to the residue, and the product was extracted with dichloromethane. Pure product was obtained by silica gel column chromatography (hexane/ether, 3/2): 1.908 g (87.5%; 4.38 mmol); mp 164–164.4 °C dec; (ethanol); ^1H NMR ($CDCl_3$) δ 2.07–2.70 (m containing s at 2.43, 9 H), 3.25 (s, 2 H), 3.67–4.50 (m, 4 H), 7.10–7.37 (m containing s at 7.23, 7 H), 7.93 (d, J = 9 Hz, 2 H); IR (KBr) 1325, 1305 (SO_2 asymmetrical), 1135, 1110 cm^{-1} (SO_2 symmetrical); MS, m/z 437 ($M^{\cdot+}$ + 1). Anal. Calcd for $C_{21}H_{24}O_6S_2$: C, 57.78; H, 5.45. Found: C, 57.52; H, 5.47.

7-Allyl-7-(*p*-tolylsulfonyl)-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-Dioxide (15c). An acetone solution (30 mL) of **14** (1.73 g, 5.0 mmol), allyl bromide (1.21 g, 10.0 mmol), and potassium carbonate (2.07 g, 15.0 mmol) was refluxed for 20 h. After acetone was removed under vacuum, water was added to the residue and the product was extracted with dichloromethane. The di-

chloromethane extract was washed with water, dried over magnesium sulfate, and concentrated to give a solid: 1.88 g (97%); mp 150.2–151.4 °C dec (ethanol); ^{1}H NMR ($CDCl_3$) δ 2.00–2.60 (m containing s at 2.43, 7 H), 2.67–3.10 (m, 2 H), 3.34 (t, J = 6 Hz, 1 H), 3.73 (t, J = 6 Hz, 1 H), 3.90–4.20 (m, 4 H), 4.87–5.40 (m, 2 H), 5.57–6.38 (m, 1 H), 7.30 (d, J = 8 Hz, 2 H), 7.93 (d, J = 8 Hz, 2 H); IR (KBr) 1325, 1305 (SO_2 asymmetrical), 1135, 1110 cm^{-1} (SO_2 symmetrical); MS, m/z 386 ($M^{\bullet+}$). Anal. Calcd for $C_{17}H_{22}O_6S_2$: C, 52.83; H, 5.74. Found: C, 53.09; H, 5.82.

7-*n*-Pentyl-7-(*p*-tolylsulfonyl)-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-Dioxide (15d). Sodium hydride (132 mg, 5.50 mmol, 50% dispersion in mineral oil–washed with pentane) was added to a solution of **14** (1.73 g, 5.0 mmol) in dry DMF (25 mL) at room temperature with stirring under N_2 atmosphere. After the evolution of hydrogen stopped, a DMF solution (5 mL) of 1-iodopentane (1.98 g, 10.0 mmol) was added, and the reaction mixture was stirred for 20 h at 70 °C. The dark brown reaction mixture was cooled to 0 °C, quenched with water, and extracted with chloroform (30 mL × 3). The chloroform extracts were combined, washed with water, 10% sodium thiosulfate, and water, and dried over sodium sulfate. Filtration and solvent evaporation gave a solid, which was purified by column chromatography (chloroform/ethyl acetate, 39/1): yield, 1.79 g (86%); mp 107.6 °C dec; ^{1}H NMR ($CDCl_3$) δ 0.60–4.30 (m containing s at 2.43, 24 H), 7.30 and 7.90 (A_2B_2 m, J = 9 Hz, 4 H); IR (KBr) 1330, 1315 (SO_2 asymmetrical), 1140, 1110 cm^{-1} (SO_2 symmetrical), MS, m/e 416 ($M^{\bullet+}$). Anal. Calcd for $C_{19}H_{28}O_6S_2$: C, 54.78; H, 6.78. Found: C, 54.65; H, 6.68.

7-(2-Phenylethyl)-7-(*p*-tolylsulfonyl)-1,4-dioxa-8-thiaspiro[4.5]decane 8,8-Dioxide (15f). Sodium hydride (125 mg, 5.0 mmol) was added to a solution of **14** (1.43 g, 4.12 mmol) in dry DMF (30 mL) at room temperature with stirring under N_2 atmosphere. After the mixture was stirred for 0.5 h, (2-bromoethyl)benzene (1.496 g, 8.1 mmol) was added to the above solution, and the stirring was continued for 39 h at room temperature and for 6 h at 70 °C. The reaction mixture was poured into water (50 mL), and the product was extracted with chloroform (60 mL × 2). The chloroform solution was washed with water (50 mL × 5) and dried over sodium sulfate. The solid was recrystallized from ethanol; yield, 1.03 g (56%; 2.3 mmol); mp 168.5–169.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.20–3.10 (m containing s at 2.40, 11 H), 3.30 (t, J = 9 Hz, 2 H), 4.03 (s, 4 H), 7.00–7.33 (m, 7 H), 7.92 (d, J = 9 Hz, 2 H); IR (KBr) 1325, 1310 (SO_2 asymmetrical), 1140, 1130 cm^{-1} (SO_2 symmetrical); MS, m/z 451 ($M^{\bullet+}$). Anal. Calcd for $C_{22}H_{26}O_6S_2$: C, 58.65; H, 5.82. Found: C, 58.75; H, 5.80.

7-[5-(Methoxycarbonyl)pentyl]-7-(*p*-tolylsulfonyl)-1,4-dioxaspiro[4.5]decane 8,8-Dioxide (15e). Sodium hydride (13.2 mg, 0.55 mmol) was added to a solution of **14** (173 mg, 0.50 mmol) in dry DMF (10 mL) at room temperature with stirring under N_2 atmosphere. After 1 h, to the above solution was added methyl 6-iodohexanoate (256 mg, 1.00 mmol) and the mixture was stirred for 67 h at 60 °C. The reaction mixture was poured into ice–water, and the alkylated product was extracted with dichloromethane (20 mL × 3). The dichloromethane extract was washed with water (×2), sodium thiosulfate, and water (×2) and dried over magnesium sulfate. After removal of solvent under vacuum, crude solid was recrystallized from ethanol: yield, 219 mg (93%); mp 132.9–134.3 °C; ^{1}H NMR ($CDCl_3$) δ 0.97–3.10 (m containing s at 2.43, 17 H), 3.13–3.80 (m containing s at 3.63, 5 H), 3.90–4.20 (m, 4 H), 7.32 and 7.90 (d, J = 8 Hz, 4 H); IR (KBr) 1730 (C=O), 1320, 1310 (SO_2 asymmetrical), 1130, 1120 cm^{-1} (SO_2 symmetrical); MS, m/z 474 ($M^{\bullet+}$). Anal. Calcd for $C_{21}H_{30}O_8S_2$: C, 53.15; H, 6.37. Found: C, 53.21; H, 6.34.

1,4-Dioxa-7-methylspiro[4.4]non-7-ene (16a). Sodium hydride (144 mg, 6.0 mmol) and potassium hydride (8 mg, 0.2 mmol) were added to a solution of **15a** (720 mg, 2.0 mmol) in dry Me_2SO (11 mL) at room temperature with stirring under N_2 atmosphere. The reaction mixture was stirred for 48 h at room temperature and poured into water, and the product was extracted with pentane. The pentane extract was washed with water and brine and dried over sodium sulfate. Filtration and solvent evaporation gave 168 mg (60%) of an oil, which was mostly pure **16a**: ^{1}H NMR ($CDCl_3$) δ 1.70 (br s, 3 H), 2.50 (br s, 4 H), 3.90 (s, 4 H), 5.20–5.40 (m, 1 H); MS, m/z 140.0896 (calcd for $C_8H_{12}O_2$, 140.0838).

1,4-Dioxa-7-*n*-pentylspiro[4.4]non-7-ene (16d). Sodium hydride (0.608 g, 12.5 mmol, 50% dispersion in mineral oil—washed with pentane) and potassium hydride (20 mg, 0.5 mmol) were added to a solution of **15d** (2.08 g, 5.0 mmol) in dry Me_2SO (20 mL) at room temperature (26 °C) with stirring under N_2 atmosphere. The solution was poured into ice (40 g) and extracted with pentane (100 mL × 2). The pentane extracts were combined, washed with water (50 mL × 5) and brine (50 mL) and then dried over sodium sulfate. Filtration and solvent evaporation gave 0.853 g (87%) of an oil, which was mostly pure **16d** (>94% pure, checked by GLPC, SE 30, 10%, 2-m column, 140 °C; t_r 14.7 min). The minor byproduct was 3-*n*-pentyl-3-cyclopentenone (6%, checked by GLPC): ^{1}H NMR ($CDCl_3$) δ 0.96 (br t, 3 H), 1.10–1.70 (m, 6 H), 1.80–2.60 (m, 2 H), 2.30–2.70 (m, 4 H), 3.90 (s, 4 H), 5.20–5.40 (m, 1 H); IR (neat) 3050, 1645 (C=C), 850 cm^{-1}; MS, m/z 190.1440 (calcd for $C_{12}H_{20}O_2$, 196.1463).

1,4-Dioxa-7-(2-phenylethyl)spiro[4.4]non-7-ene (16f). Sodium hydride (150 mg, 6.25 mmol) and potassium hydride (40 mg, 1 mmol) were added to a solution of **15f** (900 mg, 2.0 mmol) in dry Me_2SO (15 mL) at room temperature with stirring under N_2 atmosphere. The reaction mixture was stirred for 48 h at room temperature and poured into water, and the product was extracted with pentane. The pentane extract was washed with water and brine and dried over sodium sulfate. Filtration and solvent evaporation gave 322 mg (70%) of an oil, which was mostly pure **16f**: ^{1}H NMR ($CDCl_3$) δ 2.20–2.80 (m, 8 H), 3.83 (s, 4 H), 5.30 (br s, 1 H), 7.13 (s, 5 H); MS, m/z 230.1335 (calcd for $C_{15}H_{18}O_2$, 230.1307).

1,4-Dioxa-7-benzylspiro[4.4]non-7-ene (16b). Sodium hydride (24 mg, 1 mmol) was added to a solution of **15b** (218 mg, 0.5 mmol) in dry Me_2SO (6 mL) at room temperature and the reaction mixture was stirred at 45 °C for 22 h under N_2 atmosphere. After the reaction mixture was cooled, water was added to it, and the product was extracted with pentane to give colorless oil (31.1 mg, 0.144 mmol; 29%), which was a mixture of **16b** and its isomer **16′b** (isomer ratio was determined by GLPC; SE 30, 10%, 2-m column, 180 °C; t_r 7.3 (**16b**) and 9.1 min (**16′b**) (**16b**/**16′b** = 10:1)). Pure **16b** was obtained by column chromatography: ^{1}H NMR ($CDCl_3$) δ 2.37–2.73 (br d, 4 H), 3.40 (s, 2 H), 3.88 (s, 4 H), 5.17–5.43 (m, 1 H), 7.18 (s, 5 H); MS, m/z 216.1185 (calcd for $C_{14}H_{16}O_2$, 216.1150). **16′b** was determined by GC–MS (m/z 216 ($M^{\bullet+}$)). Pentane-insoluble solids were extracted with dichloromethane to give unreacted starting material **15b** (102 mg).

1,4-Dioxa-7-allylspiro[4.4]non-7-ene (16c). Similar procedure described above was applied for **15c** with sodium hydride in dry Me_2SO at 45 °C and cyclopentene isomer **16′c** (30%) was obtained; ^{1}H NMR ($CDCl_3$) δ 1.78 (br d, J = 6 Hz, 3 H), 2.67 (br s, 4 H), 3.93 (s, 4 H), 5.40–5.80 (m, 2 H), 6.00–6.50 (m, 1 H); MS, m/z 166 ($M^{\bullet+}$). Pentane-insoluble solids were extracted with dichloromethane to give unreacted starting material **15c** (50%).

3-Methyl-3-cyclopentenone (5a).[4d] An aqueous acetone solution (5 mL; water/acetone, 1/4) of ketal **16a** (58 mg, 0.41 mmol) and pyridinium *p*-toluenesulfonate (8 mg) was refluxed for 10 h. The cooled reaction mixture was poured into ice (3 g), and the product was extracted with pentane (30 mL × 2). The pentane extract was washed with water and dried over sodium sulfate. Filtration and solvent evaporation gave 20 mg (50%) of an oil, which was 3-methyl-3-cyclopentenone (**5a**). This low yield was partly due to the instability of **5a**: ^{1}H NMR ($CDCl_3$) δ 1.80 (br s, 3 H), 2.70–3.00 (m, 4 H), 5.60–5.80 (m, 1 H); IR (pentane) 1755 cm^{-1} (C=O); MS, m/z 96 ($M^{\bullet+}$).

3-Pentyl-3-cyclopentenone (5d). An aqueous acetone solution (10 mL; water/acetone, 1/4) of ketal **16d** (360 mg, 1.84 mmol) and pyridinium *p*-toluenesulfonate (46 mg) was refluxed for 10 h. The reaction mixture was poured into water (50 mL), and cyclopentenones were extracted with pentane (50 mL × 2). The pentane extract was washed with ice–water (30 mL × 3) and brine (30 mL) and dried over sodium sulfate. Filtration and solvent evaporation gave 263 mg (94%) of an oil, which was mostly 3-pentyl-3-cyclopentenone (**5d**). Isomer ratios of cyclopentenones were determined by GLPC (**5d**/**17d** = 82:18). **5d** was purified by column chromatography and preparative GLPC: ^{1}H NMR ($CDCl_3$) δ 0.96 (br t, 3 H), 1.00–1.80 (m, 6 H), 2.00–2.30 (m, 2 H), 5.50–5.80 (m, 1 H); IR (neat) 3050, 1745 (C=O), 1615 cm^{-1} (C=C); MS, m/z 152.1182 (calcd for $C_{10}H_{16}O$, 152.1201).

3-*n*-Pentyl-2-cyclopentenone (17d).[16] This compound was isolated by column chromatography from the above reaction mixture: ^{1}H NMR ($CDCl_3$) δ 0.90 (br t, J = 7 Hz, 3 H), 1.10–1.90

(m, 6 H), 2.20–2.70 (m, 6 H), 5.80–6.00 (m, 1 H); IR (neat) 1705 (C=O), 1615 cm^{-1} (C=C); MS, m/z 152.1172 (calcd for $C_{10}H_{16}O$, 152.1201).

3-(2-Phenylethyl)-3-cyclopentenone (5f). An aqueous acetone (10 mL; water/acetone, 1/4) of ketal **16f** (200 mg, 0.87 mmol) and pyridinium *p*-toluenesulfonate (24 mg) was refluxed for 10 h. The cooled reaction mixture was poured into ice and water, and the product was extracted with pentane (50 mL × 2). The pentane extract was washed with water (30 mL × 3) and brine (30 mL), and dried over sodium sulfate. Filtration and solvent evaporation gave 133 mg (82%, 0.72 mmol) of an oil, which was mostly 3-(2-phenylethyl)-3-cyclopentenone (**5f**). Isomer ratios of cyclopentenones were determined by GLPC (**5f**/**17f** = 85:15). **5f** was purified by column chromatography and preparative GLPC: ^1H NMR ($CDCl_3$) δ 2.20–3.10 (m, 8 H), 5.70 (m, 1 H), 7.20 (s, 5 H); IR (pentane) 1745 cm^{-1} (C=O); MS, m/z 186.1038 (calcd for $C_{13}H_{14}O$, 186.1044).

3-(2-Phenylethyl)-2-cyclopentenone (17f). This compound was isolated by column chromatography and preparative GLPC from the above reaction mixture: ^1H NMR ($CDCl_3$) δ 2.20–3.10 (m, 8 H), 5.93 (m, 1 H), 7.17 (s, 5 H); IR (pentane) 1710 cm^{-1} (C=O); MS, m/z 186.1123 (calcd for $C_{13}H_{14}O$, 186.1044).

Studies of Tertiary Amine Oxides. 9.[1] Thermal Rearrangement of 1-(4-Substituted-phenyl)piperidine *N*-Oxides to the Corresponding *N*-Hydroxylamines

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(4-Substituted-phenyl)piperidine *N*-oxides undergo a thermal rearrangement to *O*-arylhydroxylamines. Electron-withdrawing substituents are essential for the rearrangement and must be ortho or para relative to the >N–O function. The reaction has been found to be first order in substrate when rates were measured in dioxane, and the activation parameters were calculated. The order of reactivity in this rearrangement is $NO_2 \gg CN >$ COPh > COMe > COOEt > $CONH_2$. The rates correlate very well with σ^- constants and the ρ value was positive and large (+3.6) pointing to a highly polar activated complex with an electron-rich reaction center. All results strongly support an intramolecular cyclic mechanism.

Pyrolysis of tertiary amine oxides involves three main reactions. Those *N*-oxides having a β-hydrogen atom undergo an elimination reaction often known as Cope elimination[2] with the formation of an olefin and a hydroxylamine. Those *N*-oxides that lack a β-hydrogen atom undergo on pyrolysis either an isomerization known as Meisenheimer rearrangement[3] with migration of a group from N to O or a thermal deoxygenation to the corresponding tertiary amines.

The Meisenheimer isomerization is limited to certain groups. Benzyl[4] and allyl[5] groups were among the first recognized to undergo N to O shift. Groups observed later include neopentyl,[6] homoadamantyl,[7] and tetrachloropyridyl.[8] The benzene nucleus, when substituted with an electron-withdrawing group, e.g., NO_2, undergoes migration during pyrolysis of *N*,*N*-dimethylaniline *N*-oxides[9] or (2- and 4-nitrophenyl)-piperidine *N*-oxides.[10] This paper described the effect of five new substituents on the course of the rearrangement of *N*-arylpiperidine *N*-oxides.

Table I. Properties of the Amines 1

no.	yield, %	mp, C° (cryst solv)	λ_{max},[a] nm (ϵ_{max})	^1H NMR, δ[b]
1a[c]	100	103–104 (EtOH)	390 (21676), 232 (8250)	8.1 (d, 2 H, J = 9.7), 6.8 (d, 2 H, J = 9.7)
1b	96	52–54 (hexane)	298 (22870), 228 (8410)	7.4 (d, 2 H, J = 9), 6.8 (d, 2 H, J = 9)
1c	92	78–80 (petroleum ether)	322 (22320), 238 (8656)	7.4 (d, 2 H, J = 9); 6.8 (d, 2 H, J = 9)
1d	90	85–87 (EtOH–H_2O)	345 (19823), 247 (8212)	7.8 (d, 2 H, J = 9); 6.8 (d, 2 H, J = 9)
1e	90	73–75 (EtOH)	307 (22736), 227 (6990)	7.9 (d, 2 H, J = 9); 6.8 (d, 2 H, J = 9)
1f	85	192–194 (EtOH–H_2O)	295 (19690), 230 (6901)	7.9 (d, 2 H, J = 9); 6.9 (d, 2 H, J = 9)
1g	78	222–224 (benzene)	308 (24923), 230 (10250)	7.9 (d, 2 H, J = 9); 6.9 (d, 2 H, J = 9)

[a] Solvent is dioxane. [b] J values are given in hertz. [c] Data of **1a** are taken from ref 10.

Results and Discussion

Synthesis. (4-Substituted-phenyl)piperidines **1**, were prepared by the reaction of 4-substituted-fluorobenzene with piperidine (Table I). N-Oxidation of the tertiary amines to the corresponding *N*-oxides **2** was accomplished with performic acid (Scheme I).

The crystalline tertiary *N*-oxides **2** were characterized by ^1H NMR, IR, UV, and elemental analysis. The physical and spectral properties of the *N*-oxides are listed in Table II.

In the ^1H NMR spectra, in general, all protons show a considerable downfield shift compared with the same protons in the corresponding tertiary amines. Such

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