A Novel Synthesis of Methylenecyclopropane Spiro-Linked with Cycloalkanes via a Cyclization of Allylic Epoxides and Its Application to a Synthesis of Fused 3-Methylfurans[1)]

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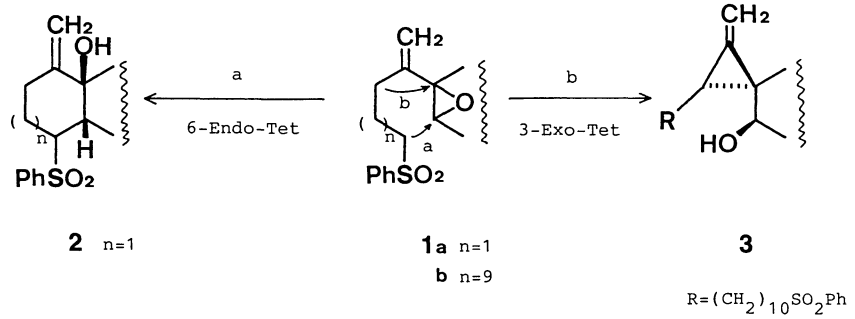
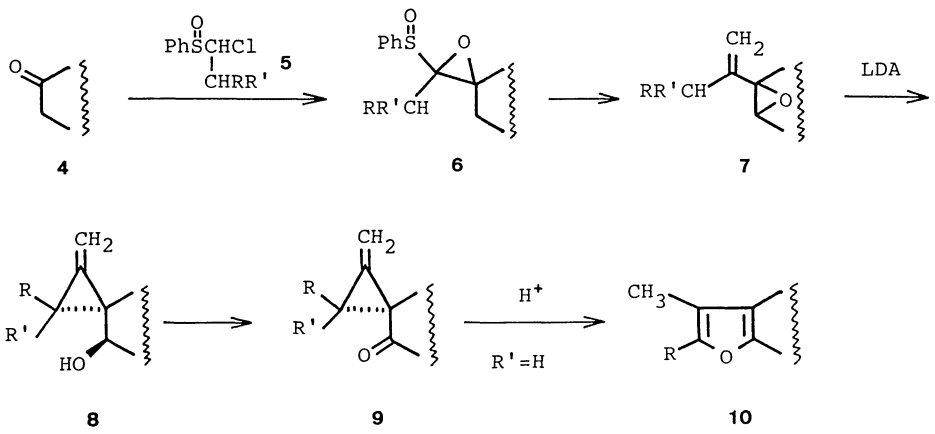
Ring closure of allylic epoxides derived from 1-chloroalkyl phenyl sulfoxides and cyclic ketones with lithium diisopropylamide (LDA) in 3-Exo-Tet mode gave spiro-linked methylenecyclopropanes having a hydroxyl group in good yields. Oxidation of these compounds gave ketones, which were then treated with *p*-toluenesulfonic acid in 1,4-dioxane or DMSO at 100 °C to give fused 3-methylfurans in good overall yields. This procedure was applied to a synthesis of menthofuran from 4-methylcyclohexanone.

Intramolecular nucleophilic ring-opening of epoxides with carbanions is one of the most useful reactions for the synthesis of carbocyclic compounds.[2)] We recently reported a new procedure for the synthesis of highly functionalized cyclohexane derivatives from ketones via epoxy sulfone cyclization.[3)] As shown in Scheme 1, treatment of the epoxy sulfone **1a** with LDA, a cyclization in 6-Endo-Tet mode[4)] took place to afford the cyclized product **2** in high yields (path a). In the study we found that treatment of **1b** with LDA did not give the 14-membered cyclized product **2b** but, instead, gave methylenecyclopropane **3** in moderate yield (path b). Clearly, from this case, the 3-Exo-Tet type reaction was shown to be easier than 14-Endo-Tet cyclization.

In this paper we would like to report in detail a novel method for the synthesis of spiro-linked methylenecyclopropanes **8** from cyclic ketones **4** and 1-chloroalkyl phenyl sulfoxides **5** through α,β-epoxy sulfoxides **7** (Scheme 2).[5)] We also report the two-step conversion of the methylenecyclopropanes **8** to cycloalkane-fused 3-methylfurans **10** via ketones **9**.



Scheme 1.

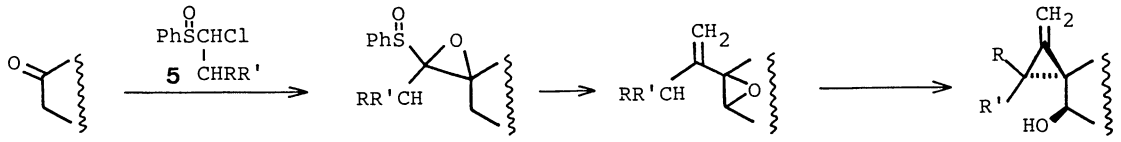


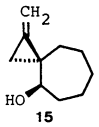
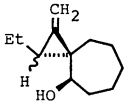
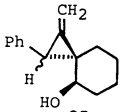
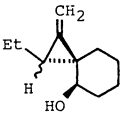
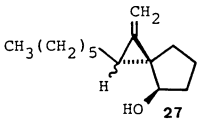
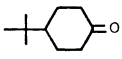
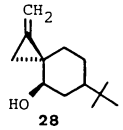
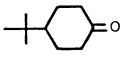
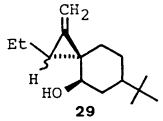
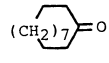
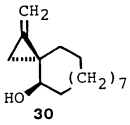
Scheme 2.

Results and Discussion

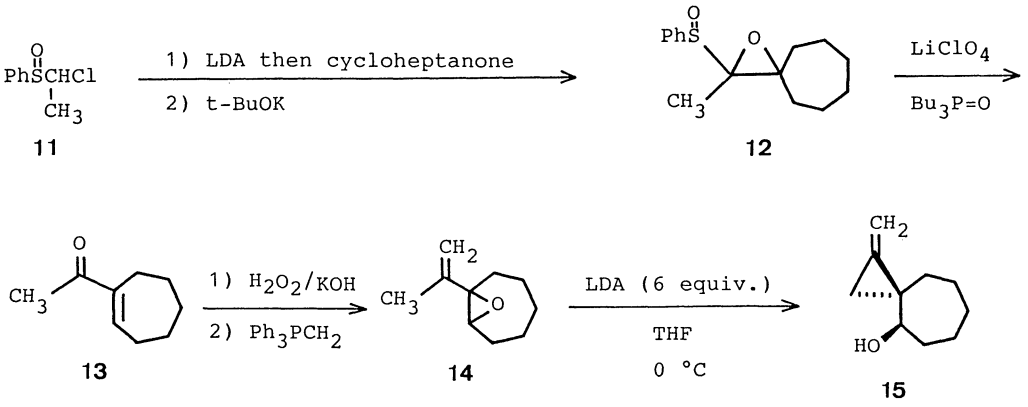
A Synthesis of Methylenecyclopropane Spiro-Linked with Cycloalkanes. Cyclopropanes are quite interesting compounds in synthetic organic chemistry and their chemistries have extensively been studied.[6] However, methylene-substituted cyclopropanes show somewhat different properties owing to their highly strained nature.[7] Some methods for the synthesis of methylenecyclopropanes and the use of these compounds in organic synthesis have been reported.[8] In perticular, the use of methylenecyclopropanes as a

Table 1. Synthesis of Methylenecyclopropane Spiro-Linked with Cycloalkanes from Cyclic Ketones and 1-Chloroalkyl Phenyl Sulfoxide **5**



Entry	Ketone	R	R′	Allylic epoxide (Yield/%)[a]	Methylenecyclopropane (Yield/%)[b]
1		H	H	**14** (70)	 **15** (88)
2		Et	H	**16** (74)	 **24** (89)[c]
3		Ph	H	**17** (43)	 **25** (99)[c]
4		Et	H	**18** (57)	 **26** (83)[c]
5		-$(CH_2)_5$-		**19** (57)	— (0)[d]
6		$CH_3(CH_2)_5$	H	**20** (70)	 **27** (91)[e]
7		H	H	**21** (50)	 **28** (93)[c]
8		Et	H	**22** (51)	 **29** (91)[c]
9		H	H	**23** (62)	 **30** (94)

a) The overall yield from the α,β-epoxy sulfoxides **6**. Isolated yield. b) The yield in the cyclization step. Isolated yield. c) Inseparable diastereomeric mixture. d) No reaction was observed. e) Separable diastereomeric mixture (ratio about 2 : 1).



Scheme 3.

precursor for trimethylenemethanes has been known.[7] However, to the best of our knowledge, no report on the synthesis of methylenecyclopropane spiro-linked with cycloalkanes has appeared so far. Here we report a novel synthesis of spiro-linked methylenecyclopropanes; the synthesis of (3*R**,4*S**)-1-methylenespiro[2.6]nonan-4-ol **15** as an example (Scheme 3).

α,β-Epoxy sulfoxide **12** was easily prepared in quantitative yield from 1-chloroethyl phenyl sulfoxide **11** and cycloheptanone through a chloro alcohol. Heating **12** with lithium perchlorate trihydrate in refluxing toluene in the presence of tributylphosphine oxide afforded enone **13** in 85% yield.[9] Epoxidation of **13** was carried out with alkaline hydrogen peroxide in methanol to give the epoxy ketone, which was then treated with methylenetriphenylphosphorane in THF to afford the allylic epoxide **14** in 91% overall yield. Cyclization of **14** to methylenecyclopropane took place cleanly with six equivalents of LDA at 0 °C for 4 h to afford **15** in 84% yield.

The structure of **15** was determined by ^{13}C NMR and IR. In ^{13}C NMR the chemical shift observed (δ=16.3, 102.6, 140.4) was characteristic of methylenecyclopropanes.[10] IR spectrum of **15** showed 3450 cm^{-1} (OH) and the characteristic vibration due to carbon-carbon double bond of methylenecyclopropanes (1760 cm^{-1}).[11] The stereochemistry of **15** was tentatively assigned on the basis of the mechanistic consideration of cyclization of **14**. Representative examples for the synthesis of spiro-linked methylenecyclopropanes from various cyclic ketones and 1-chloroalkyl phenyl sulfoxides are summarized in Table 1.

As shown in Table 1, this procedure can be applied to the synthesis of spiro-linked methylenecyclopropane or its 2-substituted derivatives. Spiro derivatives of 1-methylene-2-alkyl(or phenyl)cyclopropanes were obtained as an inseparable diastereomeric mixture with respect to the asymmetric carbon of the cyclopropane ring. The cyclization of the allylic epoxide **17** having phenyl group took place quite smoothly (the reaction was completed within 1 h) giving **25** in quantitative yield (Entry 3). This result implies that the rate of the cyclization is dependent on the acidity of the allylic hydrogen. α-(Secondary alkyl)-substituted allylic epoxide **19** did not cyclize (Entry 5).

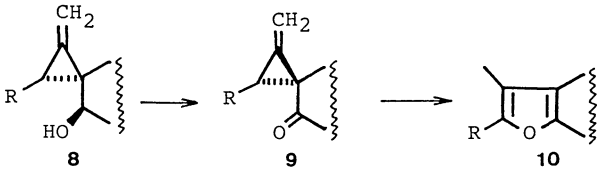
Application of the Method to the Synthesis of Fused 3-Methylfurans. It has been known that cyclopropanes in conjugation with imines undergo acid-catalyzed thermal rearrangement to afford pyrrolines.[12] Analogous with this reaction, it was anticipated that the methylenecyclopropanes in conjugation with the carbonyl group would be rearranged to methylenedihydrofurans or 3-methylfurans. In continuation of our studies with spiro-linked methylenecyclopropanes **8**, we planned to synthesize 3-methylfurans **10**, which are widely found in natural products, especially in sesquiterpenes,[13] through the methylenecyclopropane ketones **9**.[14]

Methylenecyclopropane **28** (see Table 1) was oxidized under the Swern's conditions to give methylenecyclopropane conjugated with ketone **31** in 90% yield. This ketone was quite stable under heating (in refluxing toluene for 2 h, no reaction was observed); however, with 0.3 equivalents of *p*-toluenesulfonic acid it gave the desired 3-methylfuran **34** (see Table 2) in 65% yield. Heating **31** with one equivalent of *p*-toluenesulfonic acid at 100 °C for 2 h was found to be the optimum conditions giving **34** in 84% yield. In this reaction, DMSO was similarly effective as the solvent.

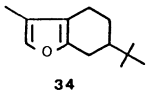
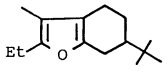
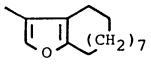
Synthesis of fused 3-methylfurans from methylenecyclopropanes through the ketones is summarized in Table 2. As shown in the table, 1-ethyl-2-methylenecyclopropane **29** gave 2-ethyl-3-methylfuran **35** in a yield similar to that of another example (Entry 2). The rate of the rearrangement was not affected by the size of the ring spiro-linked with cyclopropane (Entry 3).

Scheme 4 shows a synthesis of menthofuran **42**[15] from 4-methylcyclohexanone by the method described above. The α,β-epoxy sulfoxide **37** was synthesized from commercially available 4-methylcyclohexanone in 91% overall yield. Treatment of **37** with $LiClO_4$ gave the enone **38**, which was then epoxidized and

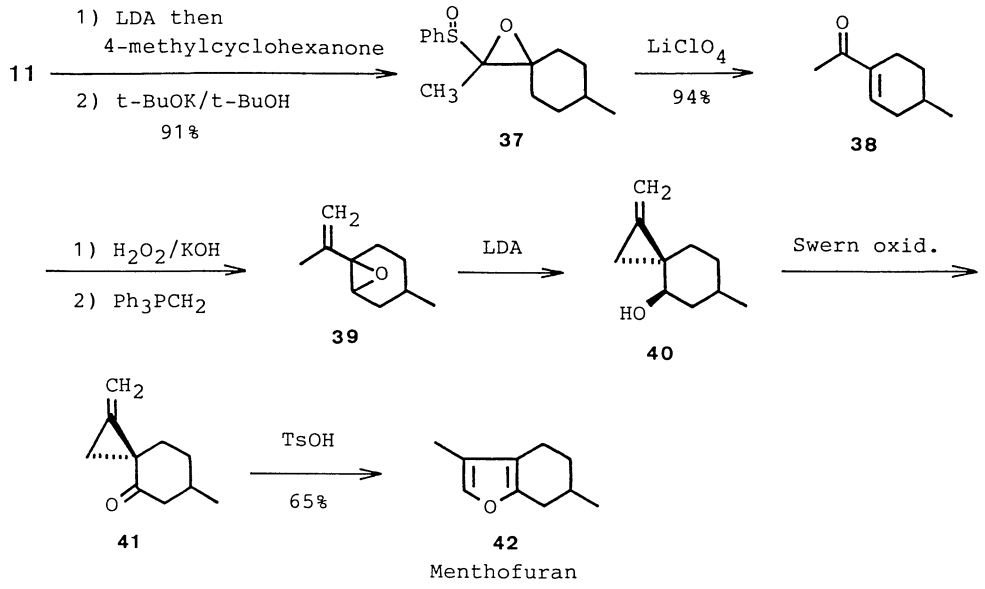
Table 2. Synthesis of Fused 3-Methylfurans **10** from Methylenecyclopropanes **8** through Ketones **9**



8 **9** **10**

Entry	Methylene-cyclopropane	Ketone (Yield/%)	Solvent[a] (Time)	3-Methylfuran (Yield/%)
1	**28**	**31** (90)	dioxane (2 h)	 (84)
				34
2	**29**	**32** (83)	dioxane (3 h)	 (58)
				35
3	**30**	**33** (99)	DMSO (3 h)	 (62)
				36

a) All reactions were carried out at 100 °C with one equivalent of *p*-toluenesulfonic acid.



Scheme 4.

methylenated to afford allylic epoxide **39** in good overall yield as a diastereomeric mixture. The cyclization took place smoothly with LDA to give methylenecyclopropane **40** (87%), which was then oxidized to give the ketone **41** in 85% yield. The rearrangement of **41** with one equivalent of *p*-toluenesulfonic acid in DMSO at 100 °C for 2 h gave menthofuran **42** (65% yield), which was identical (IR, NMR, and MS) with the authentic sample.

In conclusion, a novel synthesis of methylenecyclopropane spiro-linked with cycloalkanes and their application to fused 3-methylfurans were achieved. We believe that this study will be of value to explore further the chemistry of methylenecyclopropanes.

Experimental

All melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured in a $CDCl_3$ solution with a JEOL FX-100 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel BW-127 ZH (Fuji-Devison) containing 2% fluorescence reagent 254 and quartz column were used for column chromatography, and the products having UV absorption were detected by UV irradiation. In experiment requiring dry solvents, THF was distilled from benzophenone ketyl; diisopropylamine, toluene, and DMSO were dried over CaH_2 and distilled. All new compounds, especially oily products, did not give acceptable data for combustion analysis; however, the purity of all the title compounds was judged to be over

95% by ^{1}H NMR spectral determination and chromatographic analyses.

2′-Methyl-2′-(phenylsulfinyl)spiro[cycloheptane-1,1′-oxirane] (12). A solution of **11** (1.02 g; 5.43 mmol) in 3 ml of dry THF was added dropwise to a stirring solution of LDA (6.25 mmol) in dry THF at −60 °C under N_2. The mixture was stirred for 15 min, then cycloheptanone (6.25 mmol) was added. After 5 min the reaction was quenched with saturated aqueous NH_4Cl. The whole was extracted with ether-benzene and after the usual workup the product was purified by silica-gel column chromatography to give 1.61 g (98%) of adduct. *t*-BuOK (6.24 mmol) was added to a solution of the adduct in a mixture of *t*-BuOH-THF (3 : 1, 40 ml) and the solution was stirred at room temperature for 10 min, and then the reaction was quenched with powdered NH_4Cl. The organic solvent was evaporated and the residue was extracted with ether-benzene. The usual workup gave **12** (1.49 g; 92%) as a colorless oil. IR (neat) 1080, 1050 (SO) cm^{-1}; ^{1}H NMR δ=1.32 (3H, s), 1.4—2.0 (10H, m), 2.29 (2H, m), 7.4—7.7 (5H, m); MS *m/z* (%) 139 ([M−PhSO]$^+$ 45), 126 (46), 43 (100).

1-Acetylcycloheptene (13). A mixture of **12** (1.08 g; 4.08 mmol), $LiClO_4 \cdot 3H_2O$ (4.9 mmol), and *n*-Bu_3PO (4.1 mmol) in 40 ml of toluene was refluxed under N_2 for 45 min. The reaction mixture was diluted with benzene and was washed with water. The usual workup followed by silica-gel column chromatography gave 482 mg (85%) of the enone **13** as a colorless oil. IR (neat) 1670 (CO), 1640 cm^{-1}; ^{1}H NMR δ=1.3—1.9 (6H, m) , 2.2—2.56 (4H, m), 2.30 (3H, s), 7.05 (1H, t, *J*=6 Hz); MS *m/z* (%) 138 (M$^+$, 50), 123 (58), 95 (87), 43 (100). Found: *m/z* 138.1037. Calcd for $C_9H_{14}O$: M, 138.1043.

1-Isopropenyl-1,2-epoxycycloheptane (14). To a solution of **13** (470 mg; 3.4 mmol) in 15 ml of MeOH was added 30% H_2O_2 (1.74 ml) and 6 equiv KOH (1.02 mmol). The reaction mixture was stirred at room temperature for 3 h, then the mixture was diluted with water and the whole was extracted with CH_2Cl_2. The usual workup followed by silica-gel column chromatography afforded the epoxide 482 mg (94%) as a colorless oil; IR (neat) 1710 (CO) cm^{-1}; ^{1}H NMR δ=2.03 (3H, s), 3.22 (1H, t, *J*=6 Hz). To a mixture of methyltriphenylphosphonium iodide (1.69 g; 4.19 mmol) and *t*-BuOK (4.19 mmol) in a flame-dried flask was added 8 ml of dry THF and the yellow suspension was stirred at room temperature for 15 min. To this mixture was added a solution of the epoxide (415 mg; 2.7 mmol) and then, the reaction mixture was stirred for 30 min. The reaction was quenched with saturated aqueous NH_4Cl; then the whole was extracted with ether. The usual workup followed by silica-gel column chromatography gave **14** (409 mg; 99%) as a colorless oil. IR (neat) 1655 (C=C) cm^{-1}; ^{1}H NMR δ=1.2—2.3 (10H, m), 1.76 (3H, t, *J*=1 Hz), 2.98 (1H, t, *J*=6 Hz), 4.81 (1H, m), 4.94 (1H, m); MS *m/z* (%) 152 (M$^+$, 32), 123 (63), 109 (48), 81 (100). Found: *m/z* 152.1195. Calcd for $C_{10}H_{16}O$: M, 152.1199.

(3*R,4*S**)-1-Methylenespiro[2.6]nonan-4-ol (15).** A solution of **14** (41 mg; 0.27 mmol) in 1 ml of dry THF was added to a stirring solution of LDA (1.62 mmol) in 3 ml of dry THF at −60 °C under N_2. The mixture was stirred at −60 °C for 10 min and then at 0 °C for 4 h. The reaction was quenched with saturated aqueous NH_4Cl and the whole was extracted with ether. The usual workup followed by silica-gel column chromatography gave **15** (36 mg; 88%) as a colorless oil. IR (neat) 3450 (OH), 1760 (C=C) cm^{-1}; ^{1}H NMR δ=0.8—2.3 (13H, m), 3.38 (3H, t, *J*=6 Hz), 5.37 (1H, m), 5.49 (1H, m); ^{13}C NMR δ=16.33, 22.27, 26.66, 29.34, 30.56, 30.70, 35.82, 76.32, 102.64, 140.41; MS *m/z* (%) 152 (M$^+$, 0.5), 151 (3.5), 123 (34), 109 (91), 81 (100). Found: *m/z* 152.1197. Calcd for $C_{10}H_{16}O$: M, 152.1199.

Allylic Epoxide (16—23). These allylic epoxides were synthesized from cyclic ketones and 1-chloroalkyl phenyl sulfoxides in a similar way as described for **14**.

2-(1,2-Epoxycycloheptyl)-1-pentene (16). Colorless oil; IR (neat) 1660 cm^{-1}; ^{1}H NMR δ=0.92 (3H, t, *J*=7 Hz), 1.0—1.7 (8H, m), 1,7—2.2 (6H, m), 2.90 (1H, t, *J*=5 Hz), 4.76 (1H, m), 4.98 (1H, m); MS *m/z* (%) 180 (M$^+$, 10), 151 (100), 137 (23). Found: *m/z* 180.1520. Calcd for $C_{12}H_{20}O$: M, 180.1514.

2-(1,2-Epoxycyclohexyl)-3-phenylpropene (17). Colorless oil; IR (neat) 1640 cm^{-1}; ^{1}H NMR δ=0.8—2.1 (8H, m), 2.76 (1H, m), 3.42 (2H, bs), 4.80 (1H, m), 5.15 (1H, m), 7.18 (5H, m); MS *m/z* (%) 214 (M$^+$, 33), 185 (21), 129 (78), 91 (100). Found: *m/z* 214.1353. Calcd for $C_{15}H_{18}O$: M, 214.1355.

2-(1,2-Epoxycyclohexyl)-1-pentene (18). Colorless oil; IR (neat) 1650 cm^{-1}; ^{1}H NMR δ=0.91 (3H, t, *J*=7 Hz), 1.1—2.2 (12H, m), 2.93 (1H, m), 4.80 (1H, m), 5.02 (1H, m); MS *m/z* (%) 166 (M$^+$, 22), 137 (100), 123 (82). Found: *m/z* 166.1357. Calcd for $C_{11}H_{18}O$: M, 166.1357.

1-Cyclohexyl-1-(1,2-epoxycyclohexyl)ethylene (19). Colorless oil; IR (neat) 1620 cm^{-1}; ^{1}H NMR δ=0.8—2.2 (19H, m), 2.88 (1H, m), 4.79 (1H, m), 5.04 (1H, m); MS *m/z* (%) 206 (M$^+$, 39), 191 (8), 177 (13), 163 (100). Found: *m/z* 206.1664. Calcd for $C_{14}H_{22}O$: M, 206.1669.

2-(1,2-Epoxycyclopentyl)-1-nonene (20). Colorless oil; IR (neat) 1650 cm^{-1}; ^{1}H NMR δ=0.87 (3H, t, *J*=7 Hz), 1.0—2.1 (21H, m), 3.38 (1H, s), 4.97 (1H, m), 5.15 (1H, m); MS *m/z* (%) 208 (M$^+$, 40), 179 (10), 151 (26), 124 (100). Found: *m/z* 208.1831. Calcd for $C_{14}H_{24}O$: M, 208.1826.

2-(1,2-Epoxy-4-*t*-butylcyclohexyl)propene (21). Colorless oil; IR (neat) 1650 cm^{-1}; ^{1}H NMR δ=0.84 (9H, s), 1.0—2.3 (7H, m), 1.76 (3H, m), 3.10 (1H, bs), 4.79 (1H, m), 4.94 (1H, m); MS *m/z* (%) 194 (M$^+$, 48), 179 (25), 165 (5), 137 (82), 41 (100). Found: *m/z* 194.1669. Calcd for $C_{13}H_{22}O$: M, 194.1669.

2-(1,2-Epoxy-4-*t*-butylcyclohexyl)-1-pentene (22). Colorless oil; IR (neat) 1650 cm^{-1}; ^{1}H NMR δ=0.86 (9H, s), 0.92 (3H, t, *J*=7 Hz), 1.2—2.3 (11H, m), 3.03 (3H, bs), 4.78 (1H, m), 4.99 (1H, m); MS *m/z* (%) 222 (M$^+$, 3), 207 (6), 193 (67), 165 (74), 57 (100). Found: *m/z* 222.1985. Calcd for $C_{15}H_{26}O$: M, 222.1982.

2-(1,2-Epoxycyclododecyl)propen (23). Colorless oil; IR (neat) 1655 cm^{-1}; ^{1}H NMR δ=1.0—1.9 (20H, m), 1.89 (3H, t, *J*=1 Hz), 3.00 (1H, m), 4.85 (1H, m), 4.92 (1H, m); MS *m/z* (%) 222 (M$^+$, 25), 179 (5), 151 (6), 123 (15), 41 (100). Found: *m/z* 222.1980. Calcd for $C_{15}H_{26}O$: M, 222.1982.

Methylenecyclopropane (24—30). These methylenecyclopropanes were synthesized from the corresponding allylic epoxides in a similar way as described for **15**.

(3*R,4*S**)-2-Ethyl-1-methylenespiro[2.6]nonan-4-ol (24).** Colorless oil; IR (neat) 3425 (OH), 1745 (C=C) cm^{-1}; ^{1}H NMR δ=0.8—1.2 (4H, m), 1.2—2.2 (12H, m), 3.40 (1H, m), 5.38 (2H, m); MS *m/z* (%) 180 (M$^+$, 1), 151 (96), 137 (97), 81 (100). Found: *m/z* 180.1514. Calcd for $C_{12}H_{20}O$: M, 180.1513.

(3*R,4*S**)-1-Methylene-2-phenylspiro[2.5]octan-4-ol (25).** Colorless oil; IR (neat) 3420 (OH), 1740 (C=C) cm^{-1};

^{1}H NMR δ=0.8—2.3 (9H, m), 2.90 (1H, m), 3.60 (3/4H, m), 3.84 (1/4H, m), 5.68 (2H, m), 7.0—7.6 (5H, m); MS *m/z* (%) 214 (M^+, 58), 196 (81), 185 (99), 171 (88), 115 (100). Found: *m/z* 214.1359. Calcd for $C_{15}H_{18}O$: M, 214.1356.

(3*R,4*S**)-2-Ethyl-1-methylenespiro[2.5]octan-4-ol (26).** Colorless oil; IR (neat) 3410 (OH), 1750 (C=C) cm^{-1}; ^{1}H NMR δ=0.8—1.1 (4H, m), 1.1—2.3 (11H, m), 3.40 (1H, m), 5.36 (2H, s); MS *m/z* (%) 166 (M^+, 0.6), 151 (14), 137 (100). Found: *m/z* 166.1378. Calcd for $C_{11}H_{18}O$: M, 166.1357.

(3*R,4*S**)-2-Hexyl-1-methylenespiro[2.4]heptan-4-ol (27).** Separable two diastereomeric mixture. Clearly separated more polar isomer is reported. Colorless oil; IR (neat) 3420 (OH), 1755 (C=C) cm^{-1}; ^{1}H NMR δ=0.88 (3H, t, *J*=7 Hz), 1.0—2.1 (18H, m), 3.72 (1H, m), 5.39 (2H, bs).

(3*R,4*S**)-6-*t*-Butyl-1-methylenespiro[2.5]octan-4-ol (28).** Colorless crystals; mp 88—96 °C (AcOEt-hexane); IR (KBr) 3430 (OH), 1740 (C=C); ^{1}H NMR δ=0.88 (9H, s), 0.9—2.2 (9H, m), 3.25 (1H, bs), 5.31 (1H, m), 5.45 (1H, m); MS *m/z* (%) 191 (M^+, 1), 137 (75), 109 (100). Found: *m/z* 194.1663. Calcd for $C_{13}H_{22}O$: M, 194.1668.

(3*R,4*S**)-6-*t*-Butyl-2-ethyl-1-methylenespiro[2.5]octan-4-ol (29).** Colorless oil; IR (neat) 3420 (OH), 1755 (C=C) cm^{-1}; ^{1}H NMR δ=0.88 (9H, s), 0.9—2.1 (13H, m), 3.22 (1H, m), 5.29 (1H, m), 5.33 (1H, m); MS *m/z* (%) 222 (M^+, 33), 207 (16), 193 (60), 165 (70), 123 (66), 41 (100). Found: *m/z* 222.1982. Calcd for $C_{15}H_{26}O$: M, 222.1982.

(3*R,4*S**)-1-Methylenespiro[2.11]tetradecan-4-ol (30).** Colorless crystals; mp 64—65 °C (AcOEt-hexane); IR (KBr) 3370 (OH), 1755 (C=C) cm^{-1}; ^{1}H NMR δ=0.8—1.0 (2H, m), 1.0—2.1 (20H, m), 3.80 (1H, m), 5.37 (2H, m); Anal. Calcd for $C_{15}H_{26}O$: C, 81.08; H, 11.70%. Found: C, 81.17; H, 11.69%.

6-*t*-Butyl-1-methylenespiro[2.5]octan-4-one (31). DMSO (0.4 ml) was added dropwise to a solution of oxalyl dichloride (0.25 ml) in 8 ml of dry CH_2Cl_2 at −60 °C with stirring. The mixture was stirred for 2 min at −60 °C, then a solution of **28** (369 mg; 1.9 mmol) in 2 ml of CH_2Cl_2 was added and the mixture was stirred for 15 min. Et_3N (1.33 ml) was added to the reaction mixture and it was allowed to warm to room temperature. Water (5 ml) was added and the whole was extracted with CH_2Cl_2. The organic layer was washed successively with 5% HCl, saturated aqueous $NaHCO_3$, and saturated brine. The usual workup followed by silica-gel column chromatography gave **31** (332 mg; 90%) as a colorless oil. IR (neat) 1690 (CO) cm^{-1}; ^{1}H NMR δ=0.91 (9H, s), 1.2—2.7 (9H, m), 5.44 (2H, m); MS *m/z* (%) 192 (M^+, 41), 149 (6), 135 (20), 108 (61), 41 (100). Found: *m/z* 192.1513. Calcd for $C_{13}H_{20}O$: M, 192.1513.

6-*t*-Butyl-2-ethyl-1-methylenespiro[2.5]octan-4-one (32). Colorless oil; IR (neat) 1695 (CO) cm^{-1}; ^{1}H NMR δ=0.90 (9H, s), 1.04 (3H, t, *J*=7 Hz), 1.2—2.7 (10H, m), 5.28 (1H, d, *J*=2 Hz), 5.38 (1H, d, *J*=2 Hz); MS *m/z* (%) 220 (M^+, 24), 205 (51), 192 (56), 108 (100). Found: *m/z* 220.1824. Calcd for $C_{15}H_{24}O$: M, 220.1825.

1-Methylenespiro[2.11]tetradecan-4-one (33). Colorless oil; IR (neat) 1700 (CO) cm^{-1}; ^{1}H NMR δ=1.1—2.6 (22H, m), 5.44 (1H, m), 5.51 (1H, m); MS *m/z* (%) 220 (M^+, 14), 205 (30), 177 (63), 163 (67), 79 (100). Found: *m/z* 220.1827. Calcd for $C_{15}H_{24}O$: M, 220.1825.

Cycloalkane-Fused 3-Methylfurans (34—36). A solution of ketone **31** (63 mg; 0.33 mmol) and *p*-TsOH·H_2O (0.33 mmol) in 5 ml of 1,4-dioxane was refluxed under N_2 for 3 h. The reaction mixture was cooled, then saturated aqueous $NaHCO_3$ was added. The whole mixture was extracted with ether, and the usual workup followed by silica-gel column chromatography gave 6-*t*-butyl-3-methyl-4,5,6,7-tetrahydrobenzofuran **34** (53 mg; 84%) as a colorless oil. IR (neat) 1645, 1565 cm^{-1}; ^{1}H NMR δ=0.94 (9H, s), 1.1—2.8 (7H, m), 1.90 (3H, d, *J*=1 Hz), 7.00 (1H, m); MS *m/z* (%) 192 (M^+, 35), 177 (5), 135 (8), 108 (100). Found: *m/z* 192.1513. Calcd for $C_{13}H_{20}O$: M, 192.1513. 3-Methylfuran derivative **35**: Colorless oil; IR (neat) 1665, 1610 cm^{-1}; ^{1}H NMR δ=0.93 (9H, s), 1.16 (3H, t, *J*=7 Hz), 1.83 (3H, s), 2.53 (2H, q, *J*=7 Hz); MS *m/z* (%) 192 (M^+, 34), 135 (8), 108 (100). Found: *m/z* 192.1513: Calcd for $C_{13}H_{20}O$: M, 192.1513. 3-Methylfuran derivative **36**: Colorless oil; IR (neat) 1635, 1570 cm^{-1}; ^{1}H NMR δ=1.0—2.0 (16H, m), 1.93 (3H, d, *J*=1 Hz), 2.35 (2H, t, *J*=7 Hz), 2.54 (2H, t, *J*=7 Hz) 7.02 (1H, m); MS *m/z* (%) 220 (M^+, 92), 205 (35), 109 (100). Found: *m/z* 220.1827. Calcd for $C_{15}H_{24}O$: M, 220.1826.

A Synthesis of (±)-Menthofuran (42). (±)-Menthofuran **42** was synthesized starting from **11** and 4-methylcyclohexanone in a similar way as described above. Spectral data of the intermediates **37—41** are recorded as follows. α,β-Epoxy sulfoxide **37** (91% yield from **11**): Colorless oil; IR (neat) 1090, 1050 (SO) cm^{-1}; ^{1}H NMR δ=0.98 (3H, d, *J*=6 Hz), 1.29 (3H, s), 7.4—7.7 (5H, m); MS *m/z* (%) 264 (M^+, trace), 139 (40), 43 (100). Found: *m/z* 264.1174. Calcd for $C_{15}H_{20}O_2S$: M, 264.1182. Enone **38** (94% yield from **37**): Colorless oil; IR (neat) 1670 (CO), 1645 cm^{-1}; ^{1}H NMR δ=0.98 (3H, d, *J*=6 Hz), 2.27 (3H, s), 6.82 (1H, m); MS *m/z* (%) 138 (M^+, 81), 123 (93), 95 (88), 43 (100). Found: *m/z* 138.1044. Calcd for $C_9H_{14}O$: M, 138.1044. Epoxide **39** (69% from **38**): Colorless oil; IR (neat) 1650 cm^{-1}; ^{1}H NMR δ=0.88 (3H, d, *J*=6 Hz), 1.76 (3H, m), 3.03 (1H, m), 4.82 (1H, m), 4.96 (1H, m); MS *m/z* (%) 152 (M^+, 82), 137 (75), 41 (100). Found: *m/z* 152.1195. Calcd for $C_{10}H_{16}O$: M, 152.1199. Methylenecyclopropane **40** (87% yield from **39**): Colorless oil; IR (neat) 3370 (OH), 1745 (C=C) cm^{-1}; ^{1}H NMR δ=0.92 (3H, d, *J*=7 Hz), 0.9—2.3 (9H, m), 3.23 (1H, bs), 5.31 (1H, m), 5.45 (1H, m); MS *m/z* (%) 152 (M^+, 1), 151 (3), 137 (20), 123 (100). Found: *m/z* 152.1203. Calcd for $C_{10}H_{16}O$: M, 152.1200. Ketone **41** (85% yield from **40**): Colorless oil; IR (neat) 1705 (CO) cm^{-1}; ^{1}H NMR δ=1.05 (3H, d, *J*=6 Hz), 1.2—2.6 (9H, m), 5.40 (2H, m); MS *m/z* (%) 150 (M^+, 22), 121 (4), 108 (52), 79 (92), 39 (100). Found: *m/z* 150.1051. Calcd for $C_{10}H_{14}O$: M, 150.1044.

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