Stereoselective Synthesis of Unhindered Olefins by 2-Fold Extrusion Reactions[1]

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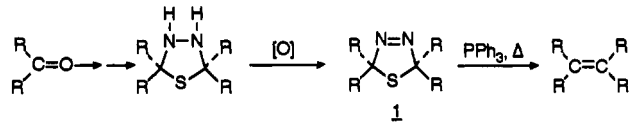
Two-fold extrusion reactions of 1,3,4-thiadiazolines 1 provide a convenient stereoselective route to unhindered *Z*-olefins. An improved preparation of the thiadiazolines involves reaction of an aldehyde with H_2S-hydrazine, followed by in situ oxidation of the intermediate predominantly trans thiadiazolidine 2. Stereospecific extrusion of nitrogen yields the *cis*-thiirane which upon treatment with triphenylphosphine affords the corresponding *Z*-alkene in good yields.

The 2-fold extrusion reaction of 1,3,4-thiadiazolines 1 was originally developed independently by Barton[2] and Kellogg[3] as a method to prepare sterically hindered alkenes. This reaction has been extensively utilized in the preparation of hindered tetrasubstituted olefins.[4,5]



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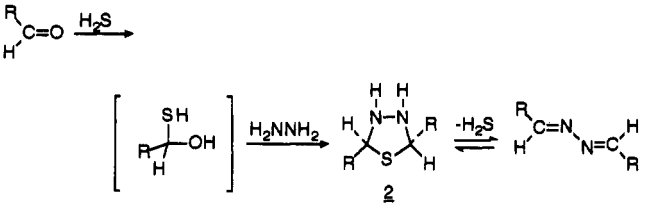
Despite the demonstrated success of 2-fold extrusion reactions in hindered cases, the reaction has not been utilized for the preparation of less hindered tri- and disubstituted alkenes. Shah[6] has reported that the 2-fold extrusion reaction of thiadiazolines does not work well for these less hindered cases; thermolysis of relatively nonhindered 1,3,4-thiadiazolines led only to low yields of thiiranes or olefins. This report was intriguing because there is no inherent mechanistic reason why the 2-fold extrusion reaction should fail in less hindered cases. Kellogg had showed that the extrusion of nitrogen from 1,3,4-thiadiazolines was stereospecific, involving a thiocarbonyl ylide intermediate.[3] The potential for controlling stereochemistry in a carbon–carbon bond-forming reaction led us to reinvestigate the synthetic utility of 2-fold extrusion reactions in less sterically hindered carbon systems.

We utilized a modified version of Rühlmann's procedure[7] for preparation of the key intermediate 1,3,4-thiadiazolidines 2. In this reaction an aldehyde is treated with H_2S gas to form a hydroxymercaptan intermediate, which quickly reacts with hydrazine to form the 1,3,4-thiadiazolidine. This procedure was found to occur much more readily than the addition of hydrogen sulfide to an azine which has been previously utilized in related extrusion reactions for thiadiazolidine preparations.[2,3] It was found that the formation and decomposition of the 1,3,4-thiadiazolidine were temperature dependent. There is an equilbrium between the 1,3,4-thiadiazolidine and the azine; in nonhindered cases at room temperature it generally takes 2 h for a solution of pure thiadiazolidine to reach an equimolar mixture of azine and thiadiazolidine. In the crystalline state at or below room temperature the thiadiazolidine is more stable and can be stored overnight without significant decomposition at −20 °C. In order to avoid significant azine formation the reaction was carried out at −30 °C for 4 h, allowing for the high-yield formation of the desired 1,3,4-thiadiazolidine.



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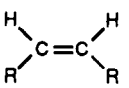
Because of the instability of the thiadiazolidine, it was decided that the oxidation of the thiadiazolidine to the thiadiazoline should best be carried out in situ without isolation in order to avoid decomposition. Extrusion of nitrogen from the thiadiazolidine occurred readily, often at room temperature over a period of a few hours. To assure complete conversion to the thiirane, the crude thiadiazoline mixtures were heated to reflux in THF or chloroform. ^1H and ^{13}C NMR of the crude thiiranes demonstrated the presence of both cis and trans isomers[8]; the cis thiirane isomer predominates (Table I).

Kellogg[3] reported that in the 2-fold extrusion reactions the overall stereochemistry of the olefin would be dictated by the geometry of the initially formed thiadiazolidine. He reported that for the hindered cases the most stable thiadiazolidine would be preferentially formed. Presumably for steric reasons this would be the trans isomer. He also proposed that extrusion of nitrogen to an intermediate thiocarbonyl ylide was followed by ring closure in a conrotatory manner, affording the more hindered *cis*-

(1) Presented at the 204th American Chemical Society National Meeting, Washington, D.C., Aug 1992, ORG 331.
(2) Barton, D. H. R.; Willis, B. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 305.
(3) Kellogg, R. M.; Buter, J.; Wassenaar, S. *J. Org. Chem.* **1972**, *36*, 4045.
(4) Guziec, F. S., Jr.; SanFilippo, L. J. *Tetrahedron* **1988**, *44*, 6241 and references cited therein.
(5) Guziec, F. S., Jr.; SanFilippo, L. J.; Murphy, C. J.; Moustakis, C. A.; Cullen, E. R. *Tetrahedron* **1985**, *41*, 4843.
(6) Shah, J. N. *Ind. J. Chem.* **1979**, *18B*, 271.
(7) Rühlmann, K. *J. Prakt. Chem.* **1959**, *8*, 285.
(8) ^1H NMR assignments were correlated with related examples taken from the literature. (a) Kondo, K.; Negishi, A. *Tetrahedron* **1971**, *27*, 4821. (b) Kondo, K.; Negishi, A.; Fukuyama, M. *Tetrahedron Lett.* **1969**, *29*, 2461.

0022-3263/93/1958-0043$04.00/0

Table I. Thiirane and Olefin Formation via 2-Fold Extrusion Reactions

RCHO		cis: trans[b]	^{1}H-NMR[c,d] δ (CHS) cis	trans	 % yield[a]	Z:E[e]
$CH_3(CH_2)_5$	75	4:1	2.95	2.62	70	4:1
$CH_3(CH_2)_8$	75	4:1	2.95	2.62	70	4:1
$CH_3(CH_2)_{10}$	62	4:1	2.96	2.64	56	4:1
	66	6:1	2.93	2.63	63	6:1
	68	6:1	2.80	2.41	64	6:1[f]

[a] Isolated yields. [b] Based on ^{1}H NMR. [c] $CDCl_3$/TMS. [d] See ref 8. [e] Based on GLC and ^{1}H NMR. [f] See ref 10.

thiirane. Sulfur extrusion would lead to retention of configuration presumably affording the *Z*-olefin.[3,9]

We found that in the less hindered cases, the *Z*-olefin was indeed the major product (Table I). On the basis of Kellogg's results, this would indicate that even in less hindered cases, the *trans*-thiadiazoline would preferentially form and decompose to the *cis*-thiirane. To confirm this assignment, 2,3-diethylthiirane was prepared using our synthetic route. The predominant product was in fact the *cis*-thiirane (cis:trans = 4:1), which corresponded spectroscopically to the previously described stereochemically pure *cis*-thiirane.[3] As expected, no loss of stereochemistry was observed when the thiiranes were desulfurized using triphenylphosphine.[9]

The stereochemistry of the product alkenes was confirmed by ^{13}C NMR spectroscopy. In general, *cis*-CH=CH- signals absorb upfield from those of the corresponding trans group.[11] For example, in the case of 10-eicosene, we found that the sp^2 carbon of the cis compound adsorbs upfield (δ 129.9), compared with the trans sp^2 carbon (δ 130.4). A much stronger shielding is experienced by the carbon atoms α to the double bound in the cis isomer due to the γ effect.[12] Consistent with this effect, the α carbon of (*Z*)-10-eicosene absorbs upfield (δ 31.9) compared to trans olefin (δ 32.7). The IR of the pure cis olefin showed an absorption band at 721 cm^{-1} which corresponds to the out of plane C-H bending vibrations for the cis disubstituted olefins. The IR of the mixture of cis and trans disubstituted olefins showed an additional absorption band at 966 cm^{-1} that is characteristic of trans disubstituted olefins.[13]

In order to obtain pure *Z*-alkenes separation of isomers was best carried out at the thiadiazolidine stage by selective crystallization of the *trans*-thiadiazolidine or at the thiirane stage by flash chromatography. In cases where the alkenes themselves might be readily separated, the crude thiadiazolidine, thiadiazoline, and thiirane mixtures were carried on without separation affording higher overall yields of the alkenes.

It is likely that the instability of the thiadiazolidines and thiadiazolines led to prior difficulties in applying 2-fold extrusion methods for the preparation of less hindered alkenes. The conditions of the 2-fold extrusion reactions are much milder than those of the Wittig reaction and provide a convenient method for the preparation of unhindered *Z*-olefins. Symmetric olefins can be prepared in moderate to good yields. Work is currently in progress to apply the 2-fold extrusion reaction to more complex asymmetrical alkenes.

Experimental Section

General experimental conditions have recently been reported.[14]

(*Z*)-10-Eicosene. The typical reaction to prepare a *Z*-alkene was carried out as follows: Freshly distilled decanal (1.4 g, 9 mmol) was placed in a cooled reaction flask with dry THF (9 mL). At -30 °C, excess H_2S gas was added using a leveling bulb-controlled burette system (analogous to that used for atmospheric pressure hydrogenation) for a period of 2 h. Concurrently, anhydrous hydrazine (1.58 g, 4.95 mmol) was added via syringe. The mixture was stirred for 4 h under the same conditions. The workup consisted of evacuating the flask (to remove excess H_2S) and washing the resulting white crystals with cold hexanes to afford the *trans*-2,5-dinonyl-1,3,4-thiadiazolidine, 1.23 g, 80% yield: mp 94–95 °C; FTIR (KBr) 3277, 2955, 2919, 2850, 1470, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.62–4.55 (t, *J* = 6 Hz, 2 H), 3.43 (m, 2 H, D_2O exchangeable), 1.84–1.26 (m, 32 H), 0.88 (t, *J* = 6 Hz, 6 H).

The thiadiazolidine was oxidized to the corresponding thiadiazoline by adding a solution of the thiadiazolidine (1.2 g, 3.5 mmol) in $CHCl_3$ (20 mL) to a suspension mixture of calcium carbonate (2.64 g, 26.4 mmol) and lead tetraacetate (2.55 g, 5.76 mmol) in $CHCl_3$ (50 mL). The mixture was stirred under a nitrogen atmosphere for a period of 2 h at -30 °C. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (24 mL). The crude mixture was filtered through Celite and then washed with saturated $NaHCO_3$ (2 × 30 mL) and water (20 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to afford the thermally unstable *trans*-2,5-dinonyl-1,3,4-thiadiazoline as a solid, 0.75 g, 62% yield: FTIR (neat) 2922, 1573, 1465, 1397 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.15 (t, *J* = 4.8 Hz, 2 H), 2.23 (m, 4 H), 1.27 (m, 28 H), 0.88 (t, *J* = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.2 (q), 22.7 (t), 26.8 (t), 29.3 (t, superimposed), 29.5 (t), 31.9 (t, superimposed), 35.7 (t), 100.1 (d).

The thiadiazoline was converted to the thiirane upon refluxing in THF (100 mL) or chloroform (100 mL) for a period of 2 h. Evaporation of the solvent gave *cis*-2,3-dinonylthiirane as a white solid, 97% yield: mp 34–35 °C; FTIR ($CHCl_3$) 2927, 2854, 1465 cm^{-1}; MS *m/z* 312.3 (M^+); ^{1}H NMR ($CDCl_3$) δ 2.95 (t, *J* = 4 Hz, 2 H), 1.83 (m, 4 H), 1.27 (m, 28 H), 0.88 (t, *J* = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.7 (t), 29.4 (t, superimposed), 29.5 (t, superimposed), 30.8 (t, superimposed), 31.9 (t), 42.1 (d).

The thiirane was desulfurized using triphenylphosphine in dry THF or neat to give the corresponding olefin. A typical reaction was carried as follows: a mixture of *cis*-2,3-dinonylthi-

(9) (a) Denney, D. B.; Boskin, M. J. *J. Am. Chem. Soc.* **1960**, *82*, 4736. (b) Neureiter, N. P.; Bordwell, F. G. *J. Am. Chem. Soc.* **1959**, *81*, 578. (c) Chan, T. H.; Finkenbine, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 2880.

(10) It appears that the tentative ^{1}H NMR assignments for (*E*)-1,2-dicyclohexylethylene and (*Z*)-1,2-dicyclohexylethylene were incorrect (Huang, J.; Goedken, V.; Walborsky, H. M. *J. Org. Chem.* **1988**, *53*, 4128). In contrast to other alkenes reported in that work, the dicyclohexylethylenes exhibit anomalous ^{1}H NMR spectra. We found that for the *Z*-isomer, the α protons absorb downfield compared to the corresponding *E*-isomer. The assignments of the vinylic protons of the isomers were also reversed in this paper. The *E*-isomer was found to absorb downfield with a small coupling constant (*J* = 3.6 Hz), and the *Z*-isomer was found to absorb upfield with a larger coupling constant (*J* = 6.2 Hz). The discrepancy in the coupling constant may be explained on the basis of steric hindrance. Our assignments of the *Z*- and *E*-isomers were confirmed by NOE and homonuclear decoupling experiments. Irradiation of either of the methine multiplets resulted in the reduction of the vinylic doublet to a singlet. However, when the low-field methine (δ = 2.32) was irradiated, the vinylic signal (δ = 5.19) increased by 15 ± 1%, whereas saturation of the high-field methine (δ = 1.92) resulted in an increase of 7 ± 1% in the intensity of the vinylic signal (δ = 5.30).

(11) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons: New York, 1981; p 261.

(12) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; Ebel, H. A., Ed.; VCH: Germany, 1987; p 193.

(13) Reference 11, p 110.

(14) Guziec, F. S., Jr.; Wei, D. *J. Org. Chem.* **1992**, *57*, 3772.

irane (1.0 g, 3.2 mmol), triphenylphosphine (1.0 g, 3.8 mmol), and THF (100 mL) was refluxed under nitrogen overnight. The mixture was cooled to room temperature, and then iodomethane (1 mL) was added. Evaporation of the solvent gave a paste which was purified by flash chromatography (silica gel, hexanes) to afford (*Z*)-10-eicosene, as a clear oil, 0.83 g, 93% yield; FTIR (neat) 3004, 2956, 2929, 2852, 1465, 1377, 721, 667 cm^{-1}; MS *m/z* 280.3 (M^+); ^1H NMR ($CDCl_3$) δ 5.365 (t, J = 4.8 Hz, 2 H), 2.022 (m, 4 H), 1.281 (m, 28 H), 0.897 (t, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.7 (t), 27.2 (t), 29.4 (t, superimposed), 29.6 (t, superimposed), 29.8 (t), 31.9 (t), 129.9 (d). Alternatively the thiirane (1.0 g, 3.2 mmol) and triphenylphosphine (1.0 g, 3.8 mmol) were heated (90 °C) under N_2 for a period of 2 h; after 1 h triphenylphosphine sulfide precipitated. The mixture was cooled to room temperature, and hexanes (20 mL) was added followed by iodomethane (1 mL). Workup was continued in the same manner affording the alkene in similar yield.

(*Z*)- and (*E*)-10-Eicosene. The typical reaction for the preparation of olefin mixture was carried as previously described for the *Z*-alkene; however, the thiadiazolidine mixture was not isolated. It was found that oxidation of the thiadiazolidine to the thiadiazoline could be carried out in higher yields if it is done without isolating the thiadiazolidine, avoiding conversion of some of the thiadiazolidine to the corresponding azine.

A typical reaction was carried out as follows: Without further purification, dry $CHCl_3$ (50 mL) was added to the previously described crude thiadiazolidine solution in THF followed by anhydrous $MgSO_4$ (1.0 g). The mixture was stirred at −30 °C under N_2 for a period of 30 min to remove any residual H_2S. To this mixture was added calcium carbonate (3.3 g, 33 mmol) and lead tetracetate (3.2 g, 7.2 mmol). The mixture was stirred for 2 h. The workup was carried out as previously described. The overall yield of the thiadiazoline mixture was 77%.

An alternate oxidation procedure was carried out using $BaMnO_4$.[5] The crude thiadiazolidine in THF solution was added to dry $CHCl_3$ (50 mL) containing anhydrous $MgSO_4$ (1.0 g) and stirred for 30 min at −30 °C. Calcium oxide (2.2 g, 39.6 mmol), sand (5.5 g), and barium manganate (5.5 g, 21.5 mmol) were added; after 2 h of stirring the mixture was filtered through Celite and the solvent was evaporated under reduced pressure, affording the thiadiazoline in similar yield. Longer reaction times in the oxidations lowered the yields; 2-h reaction time using a mechanical stirrer gave the optimum yields.

The thiadiazoline mixture was converted to the corresponding thiiranes upon refluxing in THF (100 mL) or $CHCl_3$ (100 mL), and the pure *cis*- and *trans*-2,3-dinonylthiirane mixture was obtained as an oily solid after flash column chromatography (silica gel, CCl_4), 98% yield; cis:trans = 4:1. Spectra showed the presence of the previously described cis-isomer as well as that of the trans compound. *trans*-2,3-Dinonylthiirane: ^1H NMR ($CDCl_3$) δ 2.62 (t, J = 2 Hz, 2 H), 1.94–1.70 (m, 4 H), 1.66–1.22 (m, 28 H), 0.98–0.82 (t, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.7 (t), 29.2 (t), 29.3 (t), 29.4 (t, superimposed), 29.6 (t, superimposed), 36.4 (t), 44.2 (d).

The thiirane mixture was desulfurized as previously described for the cis compound. Spectra showed the presence of the previously described *Z*-isomer as well as that of the *E*-isomer, 92% yield; *Z*:*E* = 4:1. (*E*)-10-Eicosene: ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.8 (t), 27.3 (t), 29.2 (t), 29.4 (t), 29.6 (t), 29.7 (t), 29.9 (t), 32.7 (t), 130.4 (d).

***cis*- and *trans*-2,3-Dihexylthiirane.** Prepared as described for *cis*- and *trans*-2,3-dinonylthiirane, 75% yield; cis:trans = 4:1: FTIR (neat) 2926, 2854, 1466 cm^{-1}; MS *m/z* 228.1 (M^+).

cis-2,3-Dihexylthiirane: ^1H NMR ($CDCl_3$) δ 2.95 (t, J = 4 Hz, 2 H), 1.94–1.18 (m, 20 H), 0.98–0.82 (t, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.6 (t), 29.1 (t), 29.6 (t), 30.9 (t), 31.8 (t), 42.1 (d).

trans-2,3-Dihexylthiirane: ^1H NMR ($CDCl_3$) δ 2.62 (t, J = 2 Hz, 2 H), 1.94–1.18 (m, 20 H), 0.98–0.82 (t, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.6 (t), 28.9 (t), 29.6 (t), 31.8 (t), 36.4 (t), 44.2 (d).

***cis*- and *trans*-2,3-Diundecylthiirane.** Prepared as described for *cis*- and *trans*-2,3-dinonylthiirane, 62% yield; cis:trans = 4:1: mp 43–44 °C; FTIR (KBr) 2918, 2848, 1471, 729, 614 cm^{-1}; MS *m/z* 368.3 (M^+). Anal. Calcd for $C_{24}H_{48}S$: C, 78.18; H, 13.12; S, 8.70. Found: C, 77.88; H, 13.02; S, 9.10.

cis-2,3-Diundecylthiirane: ^1H NMR ($CDCl_3$) δ 2.96 (t, J = 4 Hz, 2 H), 2.72–1.94 (m, 4 H), 1.64–1.22 (m, 36 H), 0.96–0.82 (t, J = 6 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.7 (t), 29.2 (t), 29.3 (t), 29.4 (t), 29.4 (t), 29.6 (t), 29.7 (t), 29.7 (t), 30.9 (t), 31.9 (t), 42.1 (d).

trans-2,3-Diundecylthiirane: ^1H NMR ($CDCl_3$) δ 2.64 (t, J = 2 Hz, 2 H), 2.72–1.94 (m, 4 H), 1.64–1.22 (m, 36 H), 0.96–0.82 (t, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.7 (t), 29.2 (t), 29.3 (t), 29.4 (t), 29.4 (t), 29.6 (t), 29.6 (t), 29.6 (t), 29.7 (t), 36.4 (t), 44.2 (d).

***cis*- and *trans*-2,3-Di(3-cyclohexenyl)thiirane.** Prepared as described for *cis*- and *trans*-2,3-dinonylthiirane, 66% yield; cis:trans = 6:1: bp 114–116 °C/1.1 Torr; FTIR (neat) 3021, 2914, 2834, 1651, 1450, 1434, 648 cm^{-1}; MS *m/e* 220.0 (M^+). Anal. Calcd for $C_{14}H_{20}S$: C, 76.30; H, 9.15; S, 14.54. Found: C. 75.98; H, 9.13; S, 14.89.

cis-2,3-Di(3-cyclohexenyl)thiirane: ^1H NMR ($CDCl_3$) δ 5.69 (m, 4 H), 2.93 (m, 2 H), 2.40–1.36 (m, 14 H).

trans-2,3-Di(3-cyclohexenyl)thiirane: ^1H NMR ($CDCl_3$) δ 5.69 (m, 4 H), 2.63 (m, 2 H), 2.40–1.36 (m, 14 H).

***cis*- and *trans*-2,3-Dicyclohexylthiirane.** Prepared as described for *cis*- and *trans*-2,3-dionylthiirane, 68% yield; cis:trans = 6:1: FTIR (neat) 2922, 2847, 1448, 664 cm^{-1}; MS *m/z* 224.4 (M^+). Anal. Calcd for $C_{14}H_{24}S$: C, 74.93; H, 10.78; S, 14.29. Found: C, 75.09; H, 10.68; S, 14.23.

cis-2,3-Dicyclohexylthiirane: ^1H NMR ($CDCl_3$) δ 2.80 (m, 2 H), 2.00–1.02 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ 25.9 (t), 26.1 (t), 26.2 (t), 33.5 (t), 34.7 (t), 38.8 (d, J_{CH} = 126.6 Hz), 48.9 (d, J_{CH} = 159.4 Hz).

trans-2,3-dicyclohexylthiirane: ^1H NMR ($CDCl_3$) δ 2.41 (m, 2 H), 2.00–1.02 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ 25.8 (t), 25.9 (t), 26.3 (t), 32.5 (5), 32.9 (t), 44.5 (d, J_{CH} = 122.1 Hz), 48.7 (d).

***cis*- and *trans*-2,3-Diethylthiirane.** Prepared as described for *cis*- and *trans*-1,2-dinonylthiirane, 73% yield; cis:trans = 4:1: FTIR (neat) 2927, 2855, 1462, 1072, 900 cm^{-1}.

cis-2,3-Diethylthiirane: ^1H NMR ($CDCl_3$) δ 2.94 (t, J = 5.4 Hz, 2 H), 1.95–1.30 (m, 4 H), 1.12 (t J = 6.4 Hz, 6 H).

trans-2,3-Diethylthiirane: ^1H NMR ($CDCl_3$) δ 2.62 (t, J = 4.2 Hz, 2 H), 2.02–1.30 (m, 4 H), 1.12 (t, J = 6.8 Hz, 6 H).

The spectra of the major product corresponds to the previously described pure *cis*-thiirane.[3]

(*Z*)- and (*E*)-7-Tetradecene. Prepared as described for *cis*- and *trans*-10-eicosene, 70% yield; *Z*:*E* = 4:1: FTIR (neat) 3007, 2952, 2929, 2850, 1465, 966, 722, 677 cm^{-1}; MS *m/z* 196.1 (M^+).

(*Z*)-7-Tetradecene: ^1H NMR ($CDCl_3$) δ 5.38–5.33 (t, J = 5.4 Hz, 2 H), 2.14–1.82 (m, 4 H), 1.42–1.12 (m, 16 H), 0.98–0.74 (t, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.7 (t), 27.3 (t), 29.1 (t), 29.8 (t), 31.8 (t), 129.9 (d).

(*E*)-7-Tetradecene: ^1H NMR ($CDCl_3$) δ 5.41–5.37 (t, J = 3.6 Hz, 2 H), 2.02–1.86 (m, 4 H), 1.42–1.18 (m, 16 H), 0.98–0.82 (t, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.8 (t), 29.0 (t), 29.8 (t), 31.9 (t), 32.7 (t), 130.4 (d).

(*Z*)- and (*E*)-12-Tetracosene. Prepared as described for *cis*- and *trans*-10-eicosene, 56% yield; *Z*:*E* = 4:1 FTIR (neat) 3016, 2922, 2854, 1466, 966, 722, 667 cm^{-1}; MS *m/z* 336.4 (M^+).

(*Z*)-12-Tetracosene: ^1H NMR ($CDCl_3$) δ 5.38–5.34 (t, J = 4.5 Hz, 2 H), 2.01–1.97 (m, 4 H), 1.28 (m, 36 H), 0.89 (t, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.7 (t), 27.2 (t), 29.3 (t), 29.4 (t), 29.6 (t), 29.7 (t, superimposed), 29.7 (t), 29.8 (t), 32.0 (t), 129.9 (d).

(*E*)-12-Tetracosene:[15] ^1H NMR ($CDCl_3$) δ 5.38–5.34 (t, J = 4.5 Hz, 2 H), 2.01–1.97 (m, 4 H), 1.28 (m, 36 H), 0.89 (t, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 22.7 (t), 27.2 (t), 29.2 (t), 29.3 (t), 29.6 (t), 29.6 (t), 29.7 (t), 29.7 (t), 29.8 (t), 32.6 (t), 130.4 (d).

(*Z*)- and (*E*)-1,2-Di(3-cyclohexenyl)ethylene. Prepared as described for *cis*- and *trans*-10-eicosene, 63% yield; *Z*:*E* = 6:1: FTIR (neat) 3021, 2992, 2911, 2833, 1651, 1434, 963, 745, 651 cm^{-1}; MS *m/z* 188.1 (M^+).

(*Z*)-1,2-Di(3-cyclohexenyl)ethylene: ^1H NMR ($CDCl_3$) δ 5.68 (m, 4 H), 5.26–5.22 (dd, J = 6.4, 2.1, 2 H), 2.72–2.48 (m, 2 H), 2.20–1.22 (m, 12 H).

(*E*)-1,2-Di(3-cyclohexenyl)ethylene: ^1H NMR ($CDCl_3$) δ 5.68 (m, 4 H), 5.44–5.41 (dd, J = 3.7, 1.8, 2 H), 2.38–1.22 (m, 14 H).

(15) These spectra were consistent with those previously reported for this compound. Davis, F. A.; Chen, B. *J. Org. Chem.* **1990**, *55*, 360.

(*Z*)- and (*E*)-1,2-Dicyclohexylethylene.[10] Prepared as described for *cis*- and *trans*-10-eicosene, 64% yield; *Z*:*E* = 6:1: FTIR (neat) 2992, 2922, 2850, 1448, 1260, 966, 788, 738, 667 cm^{-1}; MS *m*/*z* 192 (M^+).

(*Z*)-1,2-Dicylohexylethylene: ^1H NMR ($CDCl_3$) δ 5.19 (dd, *J* = 6.2, 2.2 Hz, 2 H), 2.46–2.18 (m, 2 H), 1.82–0.90 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 26.0 (t), 26.1 (t), 33.8 (t), 36.6 (d), 134.2 (d).

(*E*)-1,2-Dicyclohexylethylene: ^1H NMR ($CDCl_3$) δ 5.30 (dd, *J* = 3.6, 1.5 Hz, 2 H), 1.95–0.90 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ 26.2 (t), 26.3 (t), 33.8 (t), 40.7 (d), 133.8 (d).

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of (*Z*)-10-eicosene, *trans*-2,5-dinonyl-1,3,4-thiadiazoline, *cis*-2,3-dinonylthiirane, and purified cis and trans isomer mixtures of these compounds, *cis*/*trans*-2,3-dihexylthiirane, (*Z*/*E*)-7-tetradecene, (*Z*/*E*)-12-tetracosene, (*Z*/*E*)-1,2-di(3-cyclohexenyl)ethylene, and (*Z*/*E*)-1,2-dicyclohexylethylene as well as ^1H NMR spectra of *trans*-2,5-dinonyl-1,3,4-thiadiazolidine and *cis*/*trans*-2,3-diethylthiirane (22 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.