quantitated using 1-propyl 3-chlorobenzoate as internal standard.

Identification of Formaldehyde, Piperazine, and DABCO-oxide as Products of the Reaction of 3 with DABCO. Peroxide **3a** was decomposed as described above with DABCO. To this mixture 2,4-dinitrophenylhydrazine was added, followed by the addition of deionized water. A yellow precipitate formed, which was isolated by filtration. After washing with 5% $NaHCO_3$ and water, further purification was carried out by passing a chloroform solution of the precipitate through a silica gel column. Pure formaldehyde 2,4-dinitrophenylhydrazone was eluted with chloroform and methanol (1:1): yellow crystals; 23%; mp 164-165 °C (lit. mp 166 °C); mixture mp undepressed; the hydrazone was further characterized by comparison of its ^1H NMR spectrum with that of an authentic sample.

To a 3-mL aliquot of a reaction of **3a** with DABCO were added 10 mL of H_2O and 2 mL of benzoyl chloride, followed by the addition of portions of solid NaOH. The mixture was shaken, and the addition of NaOH was continued until the solution was basic. The product was extracted with $CHCl_3$, and the $CHCl_3$ layer was washed with dilute HCl and H_2O and then dried over $CaCl_2$. Evaporation of the $CHCl_3$ yielded white crystals: mp 191 °C (lit.[46] mp 191 °C); mixture mp undepressed; and ^1H NMR spectrum identical with that of an authentic sample.

DABCO-oxide was identified by matching the NMR signals (triplets at δ 3.38 and 3.10) seen in a reaction aliquot with those of authentic DABCO-oxide admixed with 1 equiv of 3-chlorobenzoic acid in $CDCl_3$.

Identification of Formaldehyde, 10, 11, and 12, and the Absence of 2-(*N*,*N*-Dimethylamino)phenol in the Reactions of 3 with DMA. Formaldehyde was isolated as its 2,4-dinitrophenylhydrazone as described for the reaction of **3** with DABCO: mp 165-66 °C; ^1H NMR spectrum identical with that of an authentic sample.

Amides **10** and urethanes **11** were identified and quantitated by comparison with authentic samples using VPC analysis (carbowax column, 1-propyl 3-chlorobenzoate internal standard) of the neutral fractions of reaction products of **3** with DMA.

The basic fraction from the decomposition reaction of **3b** and DMA was separated as described above. The base mixture was passed through a column of silica gel and eluted with hexane-chloroform (1:1), followed by elution with hexane-acetone (1:1).

(46) Shriner, R. S.; Fuson, R. C.; Curtin, D. Y.; Morrill, T. C. *The Systematic Identification of Organic Compounds*, 6th ed.; J. Wiley and Sons: New York, 1980; p 544.

The hexane-chloroform fraction contained three components as indicated by TLC. These compounds were separated by rechromatography on silica gel, eluting with toluene-chloroform (1:2). Compound **12** eluted in the first fraction: yellow crystals; mp 90-91 °C (lit.[10b] mp 89-90 °C); ^1H NMR ($CDCl_3$) δ 6.50 and 6.90 (d and d, J = 8.4 Hz, 4 H and 4 H, arom H's), 3.65 (s, 2 H, CH_2), 2.70 (s, 12 H, NCH_3's).

Further elution with chloroform gave a low-melting solid tentatively identified as 4-(4-(*N*,*N*-dimethylamino)benzyl)-*N*-methylaniline, the desmethyl homologue of **12**: ^1H NMR ($CDCl_3$) δ 6.95-7.15 and 6.10-6.70 (m and m, 4 H and 4 H, arom H's), 3.70 (s, 2 H, CH_2), 3.45 (s, 1 H, NH), 2.87 (s, 6 H, $N(CH_3)_2$), 2.75 (s, 3 H, NCH_3).

NMR Experiments. All low-temperature spectra were recorded on the Varian XL-300 spectrometer. A solution of ~0.05 g (0.0002 mol) peroxide in 0.5 mL of $CDCl_3$ (5-mm tube) was cooled to -40 °C, 2-4 mol equiv of cooled amine (1 mole equiv in the case of amine W) was added, and the reaction was monitored on the spectrometer. Typically, spectra at -40, -30, -20, -10, 0, 10 °C, and room temperature were recorded after maintaining the reaction for 10 min or so at each temperature. (In the case of W-induced decomposition, the spectra were recorded starting from -60 °C.) The experimental conditions used for the acquisition of the spectra was 10 μs pulse-width, 4-8 scans, and 4000-Hz spectral width. $CDCl_3$ was used for the lock signal.

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Registry No. **3a**, 70458-21-8; **3b**, 70458-22-9; **5a**, 125302-96-7; **5b**, 125302-97-8; **7a**, 125302-98-9; **7b**, 125302-99-0; **7c**, 12530-00-6; **10a**, 71473-94-4; **10b**, 125303-02-8; **11a**, 125303-01-7; **11b**, 125303-03-9; Q, 100-76-5; Q oxide, 25289-67-2; W, 100-22-1; DABCO, 280-57-9; DABCO oxide, 18503-52-1; DMA, 121-69-7; *m*-$ClC_6H_4CONBu_2$, 35306-68-4; c-C_4H_7-$CONBu_2$, 125302-95-6; *N*,*N*-di-*n*-butylamine, 111-92-2; benzylcyclopropylamine, 13324-66-8; cyclobutanecarbonyl chloride, 5006-22-4.

A Route to Linear, Bridged, or Spiro Polycyclic Compounds: Sequential Use of the Intermolecular Diels-Alder Reaction and Radical Cyclization

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The intermolecular Diels-Alder reaction in which either the diene or the dienophile carries a suitably located homolyzable substituent, such as a phenylseleno group, represents a convenient method for assembly of compounds that can undergo radical cyclization. The technique can be used to generate polycyclic structures that are fused in a linear, bridged, or spiro manner. The hetero Diels-Alder version is equally versatile in this connection.

The utility of radical cyclization[1] in synthetic chemistry depends very much on the ease with which structurally complex radical precursors can be assembled, and we have evaluated a number of classical processes, such as the Ireland ester enolate rearrangement[2] and the Michael addition,[3] in this regard. The Diels-Alder reaction is especially suitable for integration with radical chemistry, although it has not yet seen extensive use for this purpose. Our experiments, which are described below,[4] and the two other publications[5] in this area, show that the Diels-Alder

(1) Curran, D. P. *Synthesis* **1988**, 417. Curran, D. P. *Synthesis* **1988**, 489. Hart, D. J. *Science* **1984**, *223*, 4639.

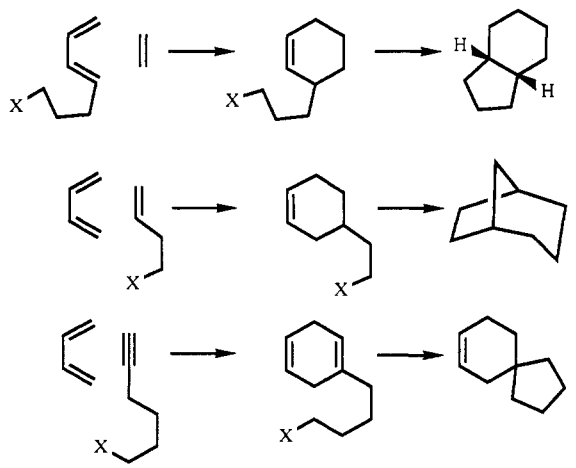
(2) Mohammed, A. Y.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 588.

(3) (a) Clive, D. L. J.; Boivin, T. L. B. *J. Org. Chem.* **1989**, *54*, 1997. (b) Clive, D. L. J.; Boivin, T. L. B.; Angoh, A. G. *J. Org. Chem.* **1987**, *52*, 4943. (c) Angoh, A. G.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 941.

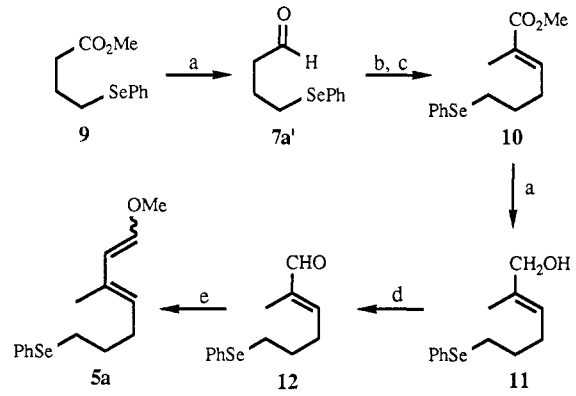
(4) This work was reported at the 72nd Canadian Chemical Conference, Victoria, B.C., 4-8 June, 1989; Abstract 604.

0022-3263/90/1955-1786$02.50/0

Scheme I



Scheme II[a]

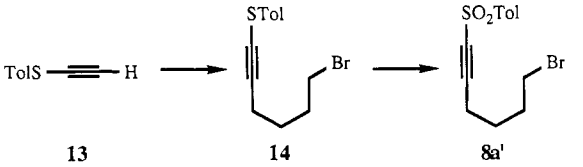


[a] (a) DIBAL; (b) $(MeO)_2P(O)CH(Me)COOMe/t$-BuOK; (c) *i*-PrSNa (catalytic); (d) DDQ; (e) $Ph_3P^+CH_2(OMe)Cl^-/t$-BuOK.

reaction provides ready access to compounds that are properly constituted to undergo radical cyclization. The two processes form a particularly felicitous combination, and the utility of the radical closure is greatly extended.

We have confined our attention to the intermolecular Diels–Alder[6] reaction including its heteroatomic[7] version. The chain carrying the radical precursor X (see Scheme I) can vary in length, and it can be located in a variety of positions on the diene or on the dienophile. We prefer to generate the required carbon radicals by homolysis of an aliphatic carbon–SePh bond. The phenylseleno group (PhSe) is easily introduced, it is sufficiently robust to survive a wide variety of reactions (except oxidation[8]), and its homolysis from an attached aliphatic substructure provides a reliable source of carbon radicals.[9] Some of the many possibilities of Diels–Alder/radical chemistry are

Scheme III



shown in Scheme I, and our results are summarized in Table I.

Both the dienes and dienophiles required for the sequences of Scheme I were obtained by standard procedures: Selenide **1a** (see Table I) was generated from (*E,E*)-octa-4,6-dienol[10] by treatment[11] with phenylselenocyanate and tributylphosphine, and the substituted selenides **5a** were accessible from ester **9**[12] by the steps shown in Scheme II. The heterodienophile **6a′** was made by reduction (diisobutylaluminum hydride) of the corresponding ester, which is a known compound.[13] Finally, acetylene **8a′** was assembled (Scheme III) by alkylation of tolylthioacetylene[14] with 1,4-dibromobutane, followed by oxidation with *m*-chloroperbenzoic acid (**13** → **14** → **8a′**).

The Diels–Alder reactions were carried out by standard methods, using thermal or catalyzed procedures, depending on the particular case (see Table I), and proceded without incident in the expected way.

For radical cyclization individual benzene solutions of triphenyltin hydride and AIBN were added over about 10 h to a refluxing solution of the substrate in the same solvent.

Radical closure of **1b** did not proceed well, but the corresponding diester **2b**, which is conformationally more mobile, gave the cyclized product in good yield. Conversion of **5b** to **5c** is an efficient process, notwithstanding the fact that here the radical closes onto the fully substituted terminus of a double bond. Such carbocyclizations are slow relative to the case in which the proximal double bond is unsubstituted,[15] but several examples are known[3a,16] in synthetic chemistry. Cyclization of **7b** to **7c** involves formation of a six-membered ring and occurs efficiently by virtue of the electron-withdrawing nature[15a] of the double bond in the starting material. Intramolecular hydrogen abstraction from C-3 (see **7b**) does not interfere.

Our results demonstrate that the Diels–Alder/radical closure sequence is a versatile route to a wide range of bicyclic compounds and merits consideration for use in the assembly of complex molecules.

Experimental Section

The same general experimental techniques were used as reported previously,[3b] except that TLC plates were usually developed with phosphomolybdic acid[17] or an acidic solution of anisaldehyde in 95% ethanol.[18]

(5) (a) Gosh, T.; Hart, H. *J. Org. Chem.* **1988**, *53*, 2396. (b) Finch, H.; Harwood, L. M.; Robertson, G. M.; Sewell, R. C. *Tetrahedron Lett.* **1989**, *30*, 2585.

(6) Onishchenko, A. S. *Diene Synthesis*; Academy of Sciences of the USSR (Engl. Transl., Israel Program for Scientific Translations: Jerusalem, 1964). Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753.

(7) Boger, D. L.; Weinreb, S. M. *Hetero Diels-Alder Methodology in Organic Synthesis*; Academic: San Diego, 1987.

(8) Chemoselective oxidation in the presence of a selenium functionality is difficult but can be accomplished: (a) Shimizu, M.; Urabe, H.; Kuwajima, I. *Tetrahedron Lett.* **1981**, *22*, 2183. (b) Posner, G. H.; Chapdelaine, M. J. *Tetrahedron Lett.* **1977**, 3227. (c) Barton, D. H. R.; Lester, D. J.; Motherwell, W. B.; Papoula, M. T. B. *J. Chem. Soc., Chem. Commun.* **1980**, 246. (d) Baudat, R.; Petrzilka, M. *Helv. Chim. Acta* **1979**, *62*, 1406. (e) Lucchetti, J.; Krief, A. *C. R. Seances Acad. Sci., Ser. C* **1979**, *288*, 537.

(9) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438.

(10) Yang, Y.-L.; Manna, S.; Falck, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 3811.

(11) Greico, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485. Sevrin, M.; Krief, A. *J. Chem. Soc., Chem. Commun.* **1980**, 656.

(12) Scarborough, R. M., Jr.; Smith, A. B., III *Tetrahedron Lett.* **1977**, 4361. Dowd, P.; Kennedy, P. *Synth. Commun.* **1981**, *11*, 935.

(13) Ley, S. V.; O'Neil, I. A.; Low, C. M. R. *Tetrahedron* **1986**, *42*, 4361.

(14) Parham, W. E.; Stright, P. L. *J. Am. Chem. Soc.* **1956**, *78*, 4783.

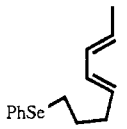
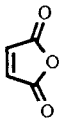
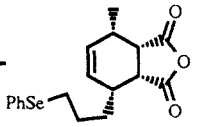
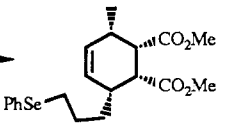
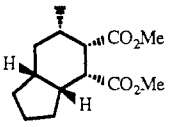
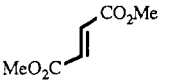
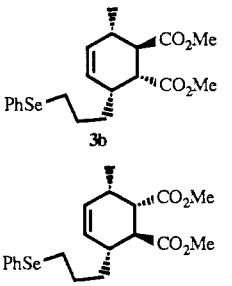
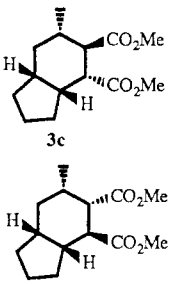
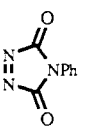
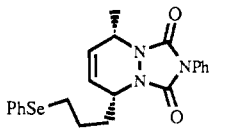
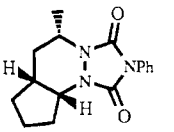
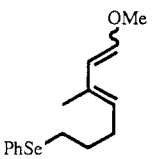
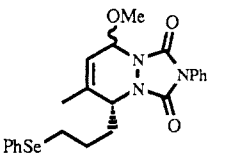
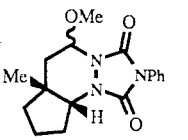
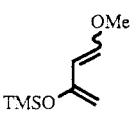
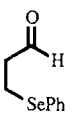
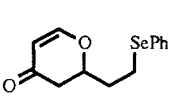
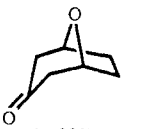
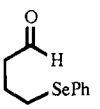
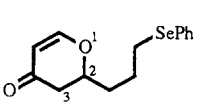
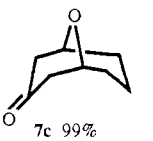
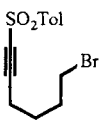
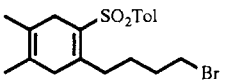
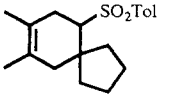
(15) (a) Beckwith, A. L.; Roberts, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 5893. (b) Beckwith, A. L.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925.

(16) Stork, G.; Reynolds, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 6911. Stork, G.; Baine N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321. Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1983**, *109*, 2829.

(17) Phosphomolybdic acid (15 g) and ceric ammonium sulfate (2.5 g) dissolved in a mixture of water (485 mL) and concentrated sulfuric acid (15 mL).

(18) Anisaldehyde (15 drops) in a mixture of 95% ethanol (94 mL) and concentrated sulfuric acid (6 mL).

Table I[a]

entry	diene	dienophile	Diels–Alder adduct	products of radical closure
1	 **1a**	 **1a'**	 **1b** 75%[b]	—
2	—	—	 **2b** 89%	 **2c** 80%
3	**3a** (= **1a**)	 **3a'**	 **3b** / **3b'** 71%[c]	 **3c** / **3c'** 94%[d]
4	**4a** (= **1a**)	 **4a'**	 **4b** 89%[e]	 **4c** 77%
5	 **5a**	**5a'** (= **4a'**)	 **5b** 73%[e]	 **5c** 77%
6	 **6a**	 **6a'**	 **6b** 57%[f] (72%)[g]	 **6c** 88%
7	**7a** (= **6a**)	 **7a'**	 **7b** 83%[f]	 **7c** 99%
8	 **8a**	 **8a'**	 **8b** 83%[h]	 **8c** 61%

[a] Yields refer to isolated materials. [b] Diels–Alder reaction done in refluxing benzene. [c] Diels–Alder reaction done in refluxing xylene. Combined yield. **3b**:**3b'** = 1:1. [d] Combined yield. **3c**:**3c'** = 1:1. [e] Diels–Alder reaction done at room temperature. [f] Diels–Alder reaction done at −78 °C in the presence of BF_3:OEt_2. [g] Yield corrected for recovered **6a'**. [h] Diels–Alder reaction done at 140 °C.

General Procedure for Radical Cyclization. The substrate was placed in a round-bottomed flask equipped with a Teflon-coated stirring bar and a reflux condenser that was sealed with a rubber septum. The system was flushed with argon for 5–10 min, and sufficient dry benzene was injected to give an approximately 0.02–0.008 M solution. The flask was lowered into an oil bath preheated to 90 °C, and dry benzene solutions of triphenyltin hydride (1.5 equiv, ca. 0.02 M) and AIBN (0.3 equiv, ca. 0.006 M) were injected simultaneously over 10 h with a double-syringe pump. Refluxing was continued for an arbitrary period

of 2 h after the end of the addition. The reaction mixture was cooled, and evaporation of the solvent gave a residue that was processed as described for the individual examples.

(*E*,*E*)-1-(Phenylseleno)octa-4,6-diene (1a). A general literature procedure[11] was followed. Tributylphosphine (0.15 mL, 122 mg, 0.602 mmol) in dry THF (3.0 mL) was added to a stirred solution of (*E*,*E*)-octa-4,6-dienol[10] (65 mg, 0.516 mmol) and phenyl selenocyanate (114 mg, 0.619 mmol) in THF (2.0 mL). The solution was stirred for 30 min and was then evaporated. Flash chromatography of the residue over silica gel (1 × 15 cm) with 1:99 ethyl acetate–hexane gave **1a** (87 mg, 64%) as an oil containing about 10% of a stereoisomer (^{1}H NMR). Compound **1a**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.72 (d, J = 6.0 Hz, 3 H), 1.79 (q, J = 7.3 Hz, 2 H), 2.17 (q, J = 7.2 Hz, 2 H), 2.9 (t, J = 7.3 Hz, 2 H), 5.35–5.65 (m, 2 H), 5.91–6.06 (m, 2 H), 7.18–7.30 (m, 3 H), 7.43–7.52 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 18.03, 27.32, 29.81, 32.51, 126.71, 127.39, 129.01, 130.29, 130.46, 131.31, 131.48, 132.57; exact mass, m/z calcd for $C_{14}H_{18}Se$ 266.0574, found 266.0571. Anal. Calcd for $C_{14}H_{18}Se$: C, 63.39; H, 6.84. Found: C, 63.54; H, 6.71.

(1α,2α,3α,6α)-6-Methyl-3-[3-(phenylseleno)propyl]-4-cyclohexene-1,2-dicarboxylic Anhydride (1b). Diene **1a** (200 mg, 0.754 mmol) and maleic anhydride (75.0 mg, 0.765 mmol) were dissolved in anhydrous benzene (5 mL), and the solution was refluxed for 6 h under argon. Evaporation of the solvent and crystallization of the residue from ethyl acetate–hexane gave **1b** (159 mg). Evaporation of the mother liquor and flash chromatography of the residue over silica gel (1 × 15 cm) with 1:3 ethyl acetate–hexane gave a further crop of **1b** (46 mg) as a white, homogeneous (^{1}H NMR) solid. The total yield of **1b** amounted to 205 mg (75%): mp 103 °C; FT-IR ($CHCl_3$ cast) 1772 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.44 (d, J = 7.2 Hz, 3 H), 1.74–2.08 (m, 4 H), 2.22 (td, J = 7.0, 5.9 Hz, 1 H), 2.42 (qd, J = 6.5, 7.2 Hz, 1 H), 2.89–3.04 (m, 2 H), 3.24 (dd, J = 6.5, 9.4 Hz, 1 H), 3.31 (dd, J = 5.9, 9.4 Hz, 1 H), 5.76 (d, J = 11 Hz, 1 H), 5.78 (d, J = 11 Hz, 1 H), 7.22–7.31 (m, 3 H), 7.47–7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 16.37, 27.38, 28.55, 30.65, 30.84, 35.68, 45.03, 46.25, 126.90, 129.13, 130.25, 132.63, 133.19, 134.97, 171.28, 171.39; exact mass, m/z calcd for $C_{18}H_{20}O_3Se$ 364.0578, found 364.0600. Anal. Calcd for $C_{18}H_{20}O_3Se$: C, 59.51; H, 5.55. Found: C, 59.57; H, 5.68.

Dimethyl (1α,2α,3α,6α)-6-Methyl-3-[3-(phenylseleno)propyl]-4-cyclohexene-1,2-dicarboxylate (2b). The Diels–Alder adduct **1b** (113 mg, 0.311 mmol) was heated for 14 h in refluxing methanol (5 mL) containing concentrated sulfuric acid (5 μL). Evaporation of the solvent and flash chromatography of the residue over silica gel (1 × 15 cm) with 1:9 ethyl acetate–hexane gave **2b** (113 mg, 89%) as a clear, homogeneous (^{1}H NMR) oil: FT-IR ($CHCl_3$ cast) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.08 (d, J = 7.5 Hz, 3 H), 1.45–1.68 (m, 2 H), 1.71–1.91 (m, 2 H), 2.34–2.44 (m, 1 H), 2.60–2.72 (m, 1 H), 2.89 (t, J = 7.4 Hz, 2 H), 3.08 (dd, J = 6.2, 4.3 Hz, 1 H), 3.03 (dd, J = 7.2, 4.3 Hz, 1 H), 3.65 (s, 3 H), 3.71 (s, 3 H), 5.56 (ddd, J = 10.0, 2.0, 1.5 Hz, 1 H), 5.63 (ddd, J = 10.0, 2.5, 2.0 Hz, 1 H), 7.19–7.30 (m, 3 H), 7.46–7.53 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 16.94, 27.73, 28.51, 30.96, 32.57, 36.84, 43.13, 45.13, 51.31, 51.43, 126.73, 127.26, 129.05, 130.58, 131.13, 132.49, 173.09, 173.33; exact mass, m/z calcd for $C_{20}H_{26}O_4Se$ 410.0996, found 410.1005. Anal. Calcd for $C_{20}H_{26}O_4Se$: C, 58.68; H, 6.40; O, 15.63. Found: C, 58.80; H, 6.55; O, 15.75.

Dimethyl (3aβ,4α,5α,6α,7aβ)-6-Methyloctahydro-1*H*-indene-4,5-dicarboxylate (2c). The general procedure for radical cyclization was followed using selenide **2b** (80 mg, 0.195 mmol) in benzene (20 mL), triphenyltin hydride (75 μL, 103 mg, 0.294 mmol) in benzene (10 mL), and AIBN (10 mg, 0.06 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (1 × 15 cm) with 1:9 ethyl acetate–hexane followed by Kugelrohr distillation gave **2c** (40 mg, 80%) as a white, homogeneous (^{1}H NMR) solid: mp 32 °C; FT-IR ($CHCl_3$ cast) 1736 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.00 (d, J = 4.9 Hz, 3 H), 1.16–1.25 (m, 1 H), 1.34–1.81 (m, 7 H), 1.90–2.03 (m, 2 H), 2.26–2.37 (m, 1 H), 2.94 (dd, J = 4.8 Hz, 1 H), 2.98 (dd, J = 5.7 Hz, 1 H), 3.65 (s, 3 H), 3.68 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.69, 22.65, 24.85, 31.35, 31.97, 33.93, 39.43, 40.16, 45.03, 45.96, 51.10, 51.62, 173.94, 174.21; exact mass, m/z calcd for $C_{14}H_{22}O_4$ 254.1518, found 254.1522. Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.36; H, 8.67.

Dimethyl (1α,2β,3β,6β)-6-Methyl-3-[3-(phenylseleno)propyl]-4-cyclohexene-1,2-dicarboxylate (3b) and Dimethyl (1α,2β,3α,6α)-6-Methyl-3-[3-(phenylseleno)propyl]-4-cyclohexene-1,2-dicarboxylate (3b′). Diene **1a** (49 mg, 0.185 mmol) and dimethyl fumarate (40 mg, 0.278 mmol) were dissolved in dry xylene (3 mL), and the solution was refluxed for 36 h. Evaporation of the solvent and flash chromatography of the residue over silica gel (1 × 15) with 1:9 ethyl acetate–hexane gave **3b** and **3b′** (54 mg, 71%) as a 1:1 mixture (^{1}H NMR) that was inseparable by chromatography: FT-IR ($CHCl_3$ cast) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.83 (d, J = 7.0 Hz, 1.5 H), 1.03 (d, J = 7.0 Hz, 1.5 H), 1.22–1.35 (m, 1 H), 1.36–1.38 (m, 0.5 H), 1.54–1.69 (m, 1.5 H), 1.71–1.91 (m, 1 H), 2.26–2.38 (m, 1 H), 2.43 (dd, J = 11.6, 10.5 Hz, 0.5 H), 2.48–2.60 (m, 0.5 H), 2.55 (dd, J = 11.0, 12.0 Hz, 0.5 H), 2.61–2.73 (m, 0.5 H), 2.78–2.92 (m, 2 H), 3.05 (dd, J = 5.5, 6.6 Hz, 0.5 H), 3.10 (dd, J = 5.5, 6.5 Hz, 0.5 H), 3.66 (s, 1.5 H), 3.68 (s, 1.5 H), 3.71 (s, 1.5 H), 3.72 (s, 1.5 H), 5.45 (ddd, J = 5.4, 1.4, 1.4 Hz, 0.5 H), 5.48 (ddd, J = 5.5, 1.5, 1.5 Hz, 0.5 H), 5.68 (ddd, J = 5.1, 5.1, 1.6 Hz, 0.5 H), 5.70 (ddd, J = 5.1, 5.1, 2.5 Hz, 0.5 H), 7.2–7.28 (m, 3 H), 7.44–7.50 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 16.82, 19.81, 25.89, 27.70, 27.74, 28.01, 31.13, 32.70, 32.93, 34.94, 35.47, 39.22, 41.79, 45.14, 46.55, 46.59, 51.69, 51.74, 126.75, 126.84, 127.94, 128.15, 129.02, 130.20, 130.41, 131.45, 131.82, 132.54, 132.73, 173.97, 176.08; exact mass, m/z calcd for $C_{20}H_{26}O_4Se$ 410.0996, found 410.1001. Anal. Calcd for $C_{20}H_{26}O_4Se$: C, 58.68; H, 6.40; O, 15.63. Found: C, 58.57; H, 6.39; O, 15.49.

Dimethyl (3aβ,4α,5β,6α,7aβ)-6-Methyloctahydro-1*H*-indene-4,5-dicarboxylate (3c) and Dimethyl (3aα,4α,5β,6β,7aα)-6-Methyloctahydro-1*H*-indene-4,5-dicarboxylate (3c′). The general procedure for radical cyclization was followed using a 1:1 mixture of **3b** and **3b′** (62 mg, 0.225 mmol) in benzene (20 mL), triphenyltin hydride (86 μL, 118 mg, 0.337 mmol) in benzene (10 mL), and AIBN (10 mg, 0.037 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (1 × 15 cm) with 7:93 ethyl acetate–hexane followed by Kugelrohr distillation gave **3c** and **3c′** (53 mg, 93%) as a 1:1 mixture (^{1}H NMR) that was inseparable by chromatography: FT-IR ($CHCl_3$ cast) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.81–0.94 (m, 0.5 H), 0.89 (d, J = 4.0 Hz, 1.5 H), 0.91 (d, J = 4.5 Hz, 1.5 H), 1.28–1.85 (m, 8 H), 1.97–2.12 (m, 1.5 H), 2.18–2.32 (m, 0.5 H), 2.36–2.47 (m, 0.5 H), 2.37 (t, J = 2.0 Hz, 0.5 H), 2.59 (t, J = 1.8 Hz, 0.5 H), 2.90 (dd, J = 11.4, 7.0 Hz, 0.5 H), 3.13 (dd, J = 11.4, 5.0 Hz, 0.5 H), 3.65 (s, 1.5 H), 3.66 (s, 1.5 H), 3.69 (s, 1.5 H), 3.70 (s, 1.5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 18.60, 20.98, 22.21, 24.42, 24.94, 30.19, 31.46, 32.08, 32.77, 34.79, 35.60, 37.06, 38.24, 40.25, 41.46, 42.89, 43.76, 46.92, 47.68, 47.90, 52.30, 52.50, 175.33, 175.47, 177.10, 177.46; exact mass, m/z calcd for $C_{14}H_{22}O_4$ 254.1518, found 254.1507. Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.35; H, 8.70.

(5α,8α)-5,8-Dihydro-8-methyl-2-phenyl-5-[3-(phenylseleno)propyl]-*s*-triazolo[1,2-*a*]pyridazine-1,3-dione (4b). Diene **1a** (32.3 mg, 0.122 mmol) in dry ether (1.5 mL) was added to the triazolinedione **4a′**[19] (24.2 mg, 0.135 mmol) in dry ether (1.0 mL). The red color of the triazolinedione was discharged instantaneously, and evaporation of the solvent followed by flash chromatography of the residue over silica gel (1 × 15 cm) with 1:3 ethyl acetate–hexane gave **4b** (43.3 mg, 81%) as a homogeneous (^{1}H NMR) oil: FT-IR ($CHCl_3$ cast) 1711 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.48 (d, J = 6.2 Hz, 3 H), 1.67–1.92 (m, 2 H), 1.95–2.07 (m, 1 H), 2.15–2.28 (m, 1 H), 2.87–3.00 (m, 2 H), 4.40–4.51 (m, 2 H), 5.73 (ddd, J = 10.0, 1.6, 0.6 Hz, 1 H), 5.81 (ddd, J = 10.0, 1.6, 0.7 Hz, 1 H), 7.24–7.34 (m, 3 H), 7.34–7.46 (m, 1 H), 7.46–7.62 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.18, 24.99, 27.50, 32.84, 50.70, 53.78, 124.38, 125.48, 127.00, 127.58, 128.01, 129.07, 129.88, 131.29, 132.96, 151.53, 152.10; exact mass, m/z calcd for $C_{22}H_{23}N_3O_2Se$ 441.0956, found 441.0958. Anal. Calcd for $C_{22}H_{23}N_3O_2Se$: C, 60.00; H, 5.26; N, 9.54; O, 7.27. Found: C, 60.04; H, 5.19; N, 9.44; O, 7.57.

(4α,5aβ,8aβ)-4-Methyldodecahydro-2-phenyl-2,3a,8b-triaza-*as*-indacene-1,3-dione (4c). The general procedure for radical cyclization was followed using **4b** (60 mg, 0.136 mmol) in benzene (25 mL), triphenyltin hydride (52 μL, 72 mg, 0.204 mmol) in

(19) Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R.; Watts, C. T. *Org. Synth.* **1986**, *51*, 121.

benzene (10 mL), and AIBN (3 mg, 0.018 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (1 × 15 cm) with 1:3 ethyl acetate–hexane gave **4c** (30.7 mg, 79%) as a homogeneous (^{1}H NMR) oil: FT-IR ($CHCl_3$ cast) 1765, 1711 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.46–1.60 (m, 2 H), 1.66 (d, J = 6.3 Hz, 3 H), 1.67–1.97 (m, 5 H), 2.08–2.17 (m, 1 H), 2.24–2.33 (m, 1 H), 3.73 (sextet of d, J = 6.3, 3.8 Hz, 1 H), 4.36 (q, J = 7.7 Hz, 1 H), 7.32–7.36 (m, 1 H), 7.44–7.54 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.22, 21.24, 25.09, 29.10, 35.29, 35.49, 52.98, 52.06, 125.66, 127.88, 129.02, 131.52, 151.82, 152.86; exact mass, m/z calcd for $C_{16}H_{19}N_3O_2$ 285.1477, found 285.1477. Anal. Calcd for $C_{16}H_{19}N_3O_2$: C, 67.35; H, 6.71; N, 14.73. Found: C, 67.27; H, 6.71; N, 14.63.

4-(Phenylseleno)butanal (7a′). Diisobutylaluminum hydride (1.0 M in dichloromethane, 17.0 mL, 17.0 mmol) was added over 5 min to a stirred and cooled (−78 °C) solution of methyl 4-(phenylseleno)butanoate[12] (**9**) (4.10 g, 15.94 mmol) in dry dichloromethane (30 mL). After 10 min, the reaction was quenched with water (30 mL) and the mixture was allowed to warm to room temperature over about 10 min. Dilute hydrochloric acid (2.0 M) was added to dissolve the precipitate, and the mixture was then extracted with ether (3 × 50 mL). The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (4 × 15 cm) with 1:9 ethyl acetate–hexane gave **7a′** (2.70 g, 75%) as a homogeneous (^{1}H NMR) oil: FT-IR ($CHCl_3$ cast) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.00 (quintet, J = 7.1 Hz, 2 H), 2.59 (td, J = 7.1, 1.0 Hz, 2 H), 2.92 (t, J = 7.1 Hz, 2 H), 7.23–7.28 (m, 3 H), 7.46–7.53 (m, 2 H), 9.74 (d, J = 1.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 22.40, 26.94, 43.43, 126.95, 129.06, 129.58, 132.67, 210.37; exact mass, m/z calcd for $C_{10}H_{12}OSe$ 228.0054, found 280.0048. Anal. Calcd for $C_{10}H_{12}OSe$: C, 52.87; H, 5.33; O, 7.04. Found: C, 52.98; H, 5.33; O, 7.04.

Methyl (*E*)-2-Methyl-6-(phenylseleno)-2-hexenoate (10). A general literature procedure[20] was followed. Methyl α-(dimethylphosphono)propionate[21] (5.70 g, 29.06 mmol) was added to a stirred and cooled (0 °C) solution of potassium *tert*-butoxide (3.26 g, 29.01 mmol) in THF (30 mL). The cooling bath was removed, and stirring was continued for 30 min. The solution was recooled to −78 °C, and aldehyde **7a′** (6.05 g, 26.63 mmol) in THF (10 mL plus 2 mL as a rinse) was added over about 2 min. The cooling bath was removed after the addition and, after 10 min, the reaction was quenched by addition of water (30 mL). The mixture was extracted with ether (3 × 50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (5 × 15 cm) with 1:25 ethyl acetate–hexane gave **10** (6.50 g, 83%) as a mixture of *Z* and *E* isomers (^{1}H NMR). This material was isomerized by a general literature procedure.[20,22] Sodium 2-propanethiolate [from 2-propanethiol (400 mg, 5.252 mmol) and sodium hydride (60% w/w in oil, 63 mg, 1.575 mmol) in DMF (4.0 mL)] was added to a solution of the above isomers (3.5 g, 11.77 mmol) in DMF (50 mL), and the mixture was heated at 90 °C for 30 min. The mixture was then cooled, quenched by addition of water (400 mL), and extracted with ether (3 × 200 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (4 × 15 cm) with 1:25 ethyl acetate–hexane gave exclusively (^{1}H NMR) the desired *E* isomer, **10** (3.01 g, 86%): FT-IR ($CHCl_3$ cast) 1716 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.83 (d, J = 1.0 Hz, 3 H), 1.83 (quintet, J = 7.4 Hz, 2 H), 2.3 (q, J = 7.5 Hz, 2 H), 2.91 (t, J = 7.2 Hz, 2 H), 3.72 (s, 3 H), 6.71 (tq, J = 7.5, 1.0 Hz, 1 H), 7.22–7.30 (m, 3 H), 7.46–7.52 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 12.46, 27.31, 28.55, 28.84, 51.71, 126.89, 128.39, 129.05, 129.97, 132.71, 140.99, 168.00; exact mass, m/z calcd for $C_{14}H_{18}O_2Se$ 298.0472, found 298.0476. Anal. Calcd for $C_{14}H_{18}O_2Se$: C, 56.57; H, 6.10; O, 10.80. Found: C, 56.66; H, 6.27; O, 10.47.

(*E*)-2-Methyl-6-(phenylseleno)-2-hexen-1-ol (11). The procedure[23] for ester **9** was followed using **10** (3.673 g, 12.356 mmol) in dichloromethane (35 mL) and diisobutylaluminum hydride (1.0 M in dichloromethane, 25.0 mL, 25.0 mmol). The reaction was quenched with water (100 mL), and the mixture was extracted with ether (3 × 100 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (4 × 15 cm) with 1:4 ethyl acetate–hexane gave **11** (2.45 g, 80%) as a homogeneous (^{1}H NMR) oil: FT-IR ($CHCl_3$ cast) 3350 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.38 (s, 1 H), 1.66 (s, 3 H), 1.78 (quintet, J = 7.0 Hz, 2 H), 2.17 (q, J = 7.2 Hz, 2 H), 2.92 (t, J = 7.0 Hz, 2 H), 4.00 (d, J = 2.8 Hz, 2 H), 5.37 (t, J = 7.2 Hz, 1 H), 7.20–7.30 (m, 3 H), 7.42–7.54 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.77, 27.51, 27.65, 29.87, 68.81, 124.81, 126.75, 129.05, 130.45, 132.59, 135.60; exact mass, m/z calcd for $C_{13}H_{18}OSe$ 270.0523, found 270.0524. Anal. Calcd for $C_{13}H_{18}OSe$: C, 57.99; H, 6.74; O, 5.94. Found: C, 57.94; H, 6.72; O, 6.10.

(*E*)-2-Methyl-6-(phenylseleno)-2-hexenal (12). A general literature procedure[8d] was followed. A solution of alcohol **11** (2.360 g, 8.765 mmol) and DDQ (2.98 g, 13.23 mmol) in dioxane (250 mL) was refluxed for 3 h, cooled, filtered through a pad of grade 3 alumina (5 × 5 cm) with ether, and evaporated. Flash chromatography of the residue over silica gel (3 × 15 cm) with 1:9 ethyl acetate–hexane gave **12** (1.71 g, 73%) as a homogeneous (^{1}H NMR) oil: FT-IR ($CHCl_3$ cast) 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.70 (s, 3 H), 1.88 (quintet, J = 5.8 Hz, 2 H), 2.47 (q, J = 5.6 Hz, 2 H), 2.94 (t, J = 7.3 Hz, 2 H), 6.44 (tq, J = 7.3, 1.2 Hz, 1 H), 7.23–7.31 (m, 3 H), 7.45–7.56 (m, 2 H), 9.39 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 9.31, 27.32, 28.76, 28.91, 127.11, 129.16, 129.53, 132.90, 140.10, 152.97, 195.06; exact mass, m/z calcd for $C_{13}H_{16}OSe$ 268.0366, found 268.0366. Anal. Calcd for $C_{13}H_{16}OSe$: C, 58.43; H, 6.04; O, 5.99. Found: C, 58.58; H, 6.20; O, 6.21.

(1*Z*,6*E*)- and (1*E*,6*E*)-1-Methoxy-3-methyl-7-(phenylseleno)hepta-1,3-diene (5a). A general literature procedure[24] was followed. Potassium *tert*-butoxide (330 mg, 2.94 mmol) was added via a side-arm addition funnel to a suspension of (methoxymethyl)triphenylphosphonium chloride (1.375 g, 3.998 mmol) in dioxane (10 mL) under argon. The mixture was stirred for 1.5 h, and then a solution of **12** (311 mg, 1.163 mmol) in dioxane (2 mL plus 1 mL as a rinse) was added over about 2 min. Stirring at room temperature was continued for 20 h. The reaction was quenched by addition of water (5 mL), and the mixture was extracted with ether (3 × 10 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm) with 1:50 ethyl acetate–hexane gave **5a** (307 mg, 89%) as a 1:1 (^{1}H NMR) mixture of isomers that were inseparable by chromatography: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.68 (s, 1.5 H), 1.70–1.84 (m, 2 H), 1.77 (s, 1.5 H), 2.22 (q, J = 7.3 Hz, 2 H), 2.90 (t, J = 7.5 Hz, 1 H), 2.91 (t, J = 7.3 Hz, 1 H), 3.57 (s, 1.5 H), 3.61 (s, 1.5 H), 5.05 (t, J = 7.3 Hz, 0.5 H), 5.22 (t, J = 7.3 Hz, 0.5 H), 5.56 (d, J = 12.7 Hz, 0.5 H), 5.85 (d, J = 13.0 Hz, 0.5 H), 6.5 (d, J = 12.7 Hz, 0.5 H), 6.58 (d, J = 13.0 Hz, 0.5 H), 7.17–7.22 (m, 3 H), 7.42–7.53 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 12.76, 20.66, 27.06, 27.46, 27.99, 30.15, 30.18, 56.42, 56.59, 103.46, 110.46, 124.78, 125.78, 126.64, 128.98, 130.30, 130.51, 130.58, 131.58, 132.43, 132.49, 146.82, 149.07; exact mass, m/z calcd for $C_{15}H_{20}OSe$ 296.0679, found 296.0664. Anal. Calcd for $C_{15}H_{20}OSe$: C, 61.01; H, 6.83; O, 5.42. Found: C, 60.88; H, 6.77; O, 6.08.

(5α,8α)- and (5α,8β)-5,8-Dihydro-5-methoxy-7-methyl-2-phenyl-8-[3-(phenylseleno)propyl]-*s*-triazolo[1,2-*a*]-pyridazine-1,3-dione (5b). Dienes **5a** (223 mg, 0.755 mmol) in ether (5 mL) were added to the triazolinedione **4a′** (162 mg, 0.904 mmol) in dry ether (5 mL). The color was discharged immediately. Evaporation of the solvent and flash chromatography of the residue over silica gel (2 × 15 cm) with 1:3 ethyl acetate–hexane gave **5b** (246 mg, 69%) as a 1:1 mixture (^{1}H NMR) of isomers that were inseparable by chromatography: FT-IR ($CHCl_3$ cast) 1785, 1714 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60–2.09 (m, 3 H), 1.83 (s, 1.5 H), 1.88 (s, 1.5 H), 2.12–2.25 (m, 0.5 H), 2.25–2.40 (m, 0.5 H), 2.76–3.10 (m, 2 H), 3.52 (s, 1.5 H), 3.58 (s, 1.5 H), 4.47

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(dd, J = 5.0, 3.0 Hz, 0.5 H), 4.54 (t, J = 4.5 Hz, 0.5 H), 5.49 (d, J = 3.0 Hz, 0.5 H), 5.51 (d, J = 4.8 Hz, 0.5 H), 5.70 (dq, J = 4.0, 1.0 Hz, 0.5 H), 5.82 (dq, J = 3.6, 0.7 Hz, 0.5 H), 7.20–7.31 (m, 3 H), 7.35–7.61 (m, 7 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.04, 20.32, 24.57, 24.99, 27.54, 27.64, 29.97, 31.92, 56.20, 56.91, 57.06, 58.14, 78.29, 80.00, 117.93, 118.39, 125.51, 126.89, 127.08, 128.21, 129.04, 120.10, 129.13, 130.06, 131.17, 131.41, 132.86, 132.90, 136.91, 137.78, 150.24, 150.47, 151.09, 152.15; exact mass, m/z calcd for $C_{23}H_{25}N_3O_3Se$ 471.1069, found 471.1064. Anal. Calcd for $C_{23}H_{25}N_3O_3Se$: C, 58.72; H, 5.36; N, 8.93; O, 10.20. Found: C, 58.91; H, 5.64; N, 8.72; O, 9.89.

(4α,5aβ,8aβ)- and (4α,5aα,8aα)-4-Methoxy-5a-methyldodecahydro-2-phenyl-2,3a,8b-triaza-*as*-indacene-1,3-dione (5c). The general procedure for radical cyclization was followed using **5b** (72 mg, 0.153 mmol) in benzene (30 mL), triphenyltin hydride (50 μL, 68 mg, 0.196 mmol) in benzene (10 mL), and AIBN (4 mg, 0.024 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (1 × 15 cm) with 1:3 ethyl acetate–hexane gave **5c** (37.2 mg, 77%) as a 1:1 mixture (^{1}H NMR) of isomers that were inseparable by chromatography: FT-IR ($CHCl_3$ cast) 1714 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.10 (s, 1.5 H), 1.36 (s, 1.5 H), 1.42–1.96 (m, 6 H), 2.07–2.24 (m, 1 H), 2.28–2.42 (m, 0.5 H), 2.48–2.60 (m, 0.5 H), 3.44 (s, 1.5 H), 3.48 (s, 1.5 H), 3.84 (dd, J = 6.3, 5.1 Hz, 0.5 H), 4.12 (t, J = 8.8 Hz, 0.5 H), 5.39 (dd, J = 4.7, 2.6 Hz, 0.5 H), 5.44 (dd, J = 3.4, 2.4 Hz, 0.5 H), 7.33–7.40 (m, 1 H), 7.45–7.55 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.54, 22.20, 24.92, 26.29, 28.84, 30.00, 35.03, 37.17, 37.70, 38.75, 39.32, 40.10, 57.30, 57.57, 62.55, 65.10, 81.04, 81.99, 125.44, 125.58, 128.02, 129.06, 131.41, 152.03, 152.97; exact mass, m/z calcd for $C_{17}H_{21}N_3O_3$ 315.1583, found 315.1584. Anal. Calcd for $C_{17}H_{21}N_3O_3$: C, 64.74; H, 6.71; N, 13.32. Found: C, 64.70; H, 6.62; N, 13.15.

3-(Phenylseleno)propanal (6a′). Methyl 3-bromopropionate (2.22 g, 13.3 mmol) in absolute ethanol (5 mL plus 1 mL as a rinse) was added to a solution of phenylselenide anion (13.4 mmol) [from $NaBH_4$ (0.51 g, 13.3 mmol) added via a side-arm addition funnel to a solution of diphenyl diselenide (2.0 g, 6.7 mmol) in absolute ethanol (50 mL)]. The mixture was stirred for 15 min and then refluxed for 2 h. The mixture was cooled, filtered, concentrated to about 10 mL, and diluted with ether (100 mL). The organic solution was washed with water (2 × 20 mL) and with brine (20 mL), dried ($MgSO_4$), and evaporated. The resulting crude methyl 3-(phenylseleno)propionate (3.018 g) was found to be about 90% pure by flash chromatography of a portion of product over silica gel (2 × 15 cm) with 2:25 ethyl acetate–hexane. The remaining crude product (2.606 g, 11.47 mmol) in dichloromethane (25 mL) was treated with diisobutylaluminum hydride (1 M in dichloromethane, 11.0 mL, 11.0 mmol) as in the procedure used for aldehyde **7a′**. The reaction was quenched with water (100 mL), and the mixture was extracted with ether (3 × 150 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (4 × 15 cm) with 2:25 ethyl acetate–hexane gave **6a′** (1.941 g, 86%) as a homogeneous (^{1}H NMR) oil: FT-IR ($CHCl_3$ cast) 1722 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.87 (td, J = 7.0, 1.0 Hz, 2 H), 3.10 (t, J = 7.0 Hz, 2 H), 7.25–7.31 (m, 3 H), 7.46–7.54 (m, 2 H), 9.73 (d, J = 1.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 18.90, 44.18, 127.40, 129.07, 129.20, 133.23, 200.61; exact mass, m/z calcd for $C_9H_{10}OSe$ 213.9897, found 213.9900. Anal. Calcd for $C_9H_{10}OSe$: C, 50.72; H, 4.73; O, 7.51. Found: C, 50.77; H, 4.73; O, 7.68.

2-[2-(Phenylseleno)ethyl]-2,3-dihydropyran-4-one (6b). A general literature procedure[25] was followed. Boron trifluoride etherate (93 μL, 0.746 mmol) was added to a stirred and cooled (−78 °C) solution of aldehyde **6a′** (159 mg, 0.746 mmol) and dienes **6a**[26] (160 mg, 0.928 mmol) in dry dichloromethane (10 mL). After 2 h at −78 °C, the reaction was quenched by addition of saturated aqueous sodium bicarbonate (5 mL), and the mixture was extracted with ether (3 × 5 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated. Trifluoroacetic acid (1% w/v in CCl_4, 10 mL) was added to the residue. After 5 min, ether (10 mL) was added, and the organic solution was washed with aqueous sodium bicarbonate (5% w/w, 5.0 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1 × 15 cm) with 1:5 ethyl acetate–hexane gave **6b** (120 mg, 57%; 72% based on conversion) as a homogeneous (^{1}H NMR) oil, along with starting aldehyde **6a′** (34 mg). Compound **6b**: FT-IR ($CHCl_3$ cast) 1677 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.85–2.06 (m, 1 H), 2.14–2.32 (m, 1 H), 2.38 (ddd, J = 16.8, 4.5, 1.1 Hz, 1 H), 2.54 (dd, J = 16.8, 12.2 Hz, 1 H), 2.91–3.16 (m, 2 H), 4.57 (octet, J = 4.1 Hz, 1 H), 5.40 (dd, J = 6.0, 1.1 Hz, 1 H), 7.20–7.36 (m, 3 H), 7.32 (d, J = 6.0 Hz, 1 H), 7.45–7.57 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 22.47, 34.65, 41.53, 78.41, 107.16, 127.20, 129.16, 129.32, 132.67, 162.79, 191.93; exact mass, m/z calcd for $C_{13}H_{14}O_2Se$ 282.1067, found 282.1030. Anal. Calcd for $C_{13}H_{14}O_2Se$: C, 55.52; H, 5.02; O, 11.38. Found: C, 55.59; H, 4.98; O, 11.62.

8-Oxabicyclo[3.2.1]octan-3-one (6c).[27] The general procedure for radical cyclization was followed using **6b** (50 mg, 0.178 mmol) in benzene (20 mL), triphenyltin hydride (90 μL, 124 mg, 0.352 mmol) in benzene (10 mL), and AIBN (5 mg, 0.03 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (1 × 15 cm) with 1:4 ethyl acetate–hexane gave **6c** (20 mg, 89%) as a homogeneous (^{1}H NMR) oil: FT-IR ($CHCl_3$ cast) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.73–1.84 (m, 2 H), 2.05–2.14 (m, 2 H), 2.3 (d, J = 16 Hz, 2 H), 2.61 (dd, J = 16.0, 5.5 Hz, 2 H), 4.73 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.46, 49.67, 74.79, 207.54; exact mass, m/z calcd for $C_7H_{10}O_2$ 126.0680, found 126.0684.

2-[3-(Phenylseleno)propyl]-2,3-dihydropyran-4-one (7b). The procedure for **6b** was followed using aldehyde **7a′** (26 mg, 0.114 mmol), dienes **6a** (45 mg, 0.261 mmol), and boron trifluoride etherate (14 μL, 0.113 mmol) in dry dichloromethane (1.0 mL) at −78 °C. Flash chromatography of the crude product over silica gel (1 × 15 cm) with 1:5 ethyl acetate–hexane gave **7b** (28 mg, 83%): FT-IR ($CHCl_3$ cast) 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.70–2.05 (m, 4 H), 2.38 (ddd, J = 16.5, 4.8, 1.0 Hz, 1 H), 2.59 (dd, J = 16.5, 12.8 Hz, 1 H), 2.86 (t, J = 7.0 Hz, 2 H), 4.31–4.58 (m, 1 H), 5.40 (dd, J = 6.0, 1.0 Hz, 1 H), 7.22–7.33 (m, 3 H), 7.33 (d, J = 6.0 Hz, 1 H), 7.45–7.57 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 25.33, 27.27, 34.17, 41.74, 78.85, 106.98, 126.97, 129.05, 129.79, 132.76, 163.00, 192.27; exact mass, m/z calcd for $C_{14}H_{16}O_2Se$ 296.0323, found 296.0322. Anal. Calcd for $C_{14}H_{16}O_2Se$: C, 56.96; H, 5.46; O, 10.84. Found: C, 56.93; H, 5.36; O, 10.97.

9-Oxabicyclo[3.3.1]nonan-3-one (7c). The general procedure for radical cyclization was followed using **7b** (53.7 mg, 0.182 mmol) in benzene (20 mL), triphenyltin hydride (95 μL, 131 mg, 0.373 mmol) in benzene (10 mL), and AIBN (5 mg, 0.03 mmol) in benzene (10 mL). Flash chromatography of the crude product over silica gel (1 × 15 cm) with 1:4 ethyl acetate–hexane gave **7c** (25.5 mg, 99%) as a homogeneous (^{1}H NMR) white solid: mp 76–80 °C; FT-IR ($CHCl_3$ cast) 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.55–1.62 (m, 4 H), 1.93–2.04 (m, 2 H), 2.36 (d, J = 16.0 Hz, 2 H), 2.78 (dd, J = 16.0, 7.3 Hz, 2 H), 4.47 (dd, J = 7.3, 4.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 15.17, 30.50, 46.03, 69.61, 208.59; exact mass, m/z calcd for $C_8H_{12}O_2$ 140.0837, found 140.0836. Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.06; H, 8.67.

6-Bromo-1-[(4-methylphenyl)thio]-1-hexyne (14). *n*-Butyllithium (1.6 M in hexanes, 3.7 mL, 5.92 mmol) was added over 5 min to a stirred solution of **13**[14] (850 mg, 5.73 mmol) in dry THF (15 mL). After 10 min, the resulting solution was added over 5 min to a stirred solution of 1,4-dibromobutane (3.70 g, 17.14 mmol) in dry THF (10 mL). The mixture was heated to 50 °C for 3 h, during which time a precipitate of lithium bromide was formed. Evaporation of the solvent followed by flash chromatography of the residue over silica gel (4 × 15 cm) with 1:99 ethyl acetate–hexane gave **14** (513 mg, 32%) as a homogeneous (^{1}H NMR) oil: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.76 (quintet, J = 7.1 Hz, 2 H), 2.00 (quintet, J = 7.0 Hz, 2 H), 2.32 (s, 3 H), 2.49 (t, J = 7.0 Hz, 2 H), 3.44 (t, J = 6.5 Hz, 2 H), 3.44 (t, J = 6.5 Hz, 2 H), 7.13 (d, J = 7.9 Hz, 2 H), 7.20 (d, J = 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.45, 20.90, 27.03, 31.65, 33.02, 66.30, 97.95, 126.23, 129.66, 129.86, 136.21; exact mass, m/z calcd for $C_{13}H_{15}{}^{81}BrS$ 284.0058,

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found 284.0048. Anal. Calcd for $C_{13}H_{15}BrS$: C, 55.13; H, 5.34; S, 11.32. Found: C, 55.15; H, 5.51; S, 11.32.

6-Bromo-1-[(4-methylphenyl)sulfonyl]-1-hexyne (8a'). A general literature procedure[28] was followed. *m*-Chloroperbenzoic acid (85%, 615 mg, 3.029 mmol) was added to a stirred and cooled (0 °C) solution of **14** (405 mg, 1.430 mmol) in chloroform (4 mL). The mixture was allowed to warm to room temperature, stirred for 16 h, taken up in ether (10 mL), and washed with saturated aqueous sodium bisulfite (2 × 5 mL), saturated aqueous sodium bicarbonate (5 mL), water (5 mL), and brine (5 mL). The organic solution was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm) with 2:5 ethyl acetate–hexane gave **8a'** (415 mg, 92%) as a homogeneous oil (^1H NMR): FT-IR ($CHCl_3$ cast) 2200 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.65–1.76 (m, 2 H), 1.86–1.94 (m, 2 H), 2.41 (t, J = 6.8 Hz, 2 H), 2.46 (s, 3 H), 3.47 (t, J = 6.8 Hz, 2 H), 7.37 (d, J = 8.0 Hz, 2 H), 7.87 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 16.12, 21.65, 25.40, 31.30, 32.36, 78.97, 95.68, 127.24, 129.69, 138.95, 145.20; exact mass, m/z calcd for $C_{13}H_{15}{}^{81}BrO_2S$ 315.9946, found 315.9939. Anal. Calcd for $C_{13}H_{15}BrO_2S$: C, 49.53; H, 4.80; O, 10.15; S, 10.17. Found: C, 49.80; H, 4.87; O, 9.99; S, 10.35.

2-(4-Bromobutyl)-4,5-dimethyl-1-[(4-methylphenyl)-sulfonyl]cyclohexa-1,4-diene (8b). Sulfone **8a'** (178 mg, 0.565 mmol) and 2,3-dimethyl-1,4-butadiene (60 mg, 0.730 mmol) were dissolved in dry benzene (3 mL). The solution was sealed in a glass tube that had been flushed with argon and was heated in an oil bath at 140 °C for 20 h. The mixture was cooled, and the solvent was evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm) with 1:9 ethyl acetate–hexane gave **8b** (187 mg, 83%) as a homogeneous (^1H NMR) oil. Crystallization from dichloromethane–hexane gave a homogeneous (^1H NMR) white solid: mp 98–102 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.54–1.72 (m, 2 H), 1.64 (broad s, 6 H), 1.92 (quintet, J = 7.1 Hz, 2 H), 2.46 (s, 3 H), 2.66 (t, J = 8.0 Hz, 2 H), 2.82 (t, J = 7.0 Hz, 2 H), 2.94 (t, J = 7.5 Hz, 2 H), 3.42 (t, J = 6.6 Hz, 2 H), 7.35 (d, J = 8.0 Hz, 2 H), 7.79 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 17.50, 17.84, 21.52, 27.08, 32.14, 32.54, 33.49, 34.16, 40.13, 121.33, 122.51, 127.09, 129.64, 131.56, 138.68, 143.85, 147.93; exact mass, m/z calcd for $C_{19}H_{25}{}^{81}BrO_2S$ 398.0735, found 398.0738. Anal. Calcd for $C_{19}H_{25}BrO_2S$: C, 57.43; H, 6.34; Br, 20.11; S, 8.07. Found: C, 57.39; H, 6.02; Br, 20.23; S, 8.09.

8,9-Dimethyl-6-[(4-methylphenyl)sulfonyl]spiro[4.5]dec-8-ene (8c). The general procedure for radical cyclization was followed using **8b** (103 mg, 0.259 mmol) in benzene (20 mL), triphenyltin hydride (100 μL, 137 mg, 0.390 mmol) in benzene (10 mL), and AIBN (6 mg, 0.036 mmol) in benzene (10 mL). The residue was taken up in ether (ca. 20 mL) and stirred with an aqueous solution (10 mL) containing an excess of potassium fluoride. The precipitated tributyltin fluoride was removed by filtration, and the ether layer was separated, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1 × 15 cm) with 1:9 ethyl acetate–hexane gave **8c** (50 mg, 61%): ^1H NMR ($CDCl_3$, 400 MHz) δ 1.48 (s, 3 H), 1.51 (s, 3 H), 1.60–1.86 (m, 8 H), 1.98–2.06 (m, 2 H), 2.12 (d, J = 10.0 Hz, 1 H), 2.36 (d, J = 10.0 Hz, 1 H), 2.43 (s, 3 H), 3.14 (t, J = 5.7 Hz, 1 H), 7.31 (d, J = 8.1 Hz, 2 H), 7.73 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 18.42, 18.91, 21.51, 23.30, 24.44, 32.05, 35.24, 38.98, 42.63, 44.75, 69.19, 121.26, 125.48, 128.45, 129.34, 137.76, 143.96; exact mass, m/z calcd for $C_{19}H_{26}O_2S$ 318.1653, found 318.1643. Anal. Calcd for $C_{19}H_{26}O_2S$: C, 71.66; H, 8.23; S, 10.07. Found: C, 71.69; H, 8.11; S, 10.05.

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Registry No. **1a**, 124781-90-4; (*E,E*)-**1a**, 124781-67-5; **1b**, 124781-80-2; **2b**, 124916-17-2; **2c**, 124781-86-8; **3a'**, 624-49-7; **3b**, 124916-18-3; **3b'**, 124781-69-7; **3c**, 124781-87-9; **3c'**, 124781-78-8; **4a'**, 4233-33-4; **4b**, 124781-81-3; **4c**, 124781-88-0; (*E*)-**5a**, 124781-70-0; (*Z*)-**5a**, 124781-75-5; **5b** (isomer 1), 124781-76-6; **5b** (isomer 2), 124781-82-4; **5c** (isomer 1), 124781-77-7; **5c** (isomer 2), 124916-19-4; (*E*)-**6a**, 54125-02-9; (*Z*)-**6a**, 124306-13-4; **6a**, 103971-83-1; **6b**, 124781-83-5; **6c**, 77745-32-5; **7a'**, 124854-74-6; **7b**, 124781-84-6; **7c**, 10469-63-3; **8a'**, 124781-79-9; **8b**, 124781-85-7; **8c**, 124781-89-1; **9**, 74785-89-0; (*E*)-**10**, 124781-71-1; (*Z*)-**10**, 124781-68-6; **11**, 124781-72-2; **12**, 124781-73-3; **13**, 66823-38-9; **14**, 124781-74-4; methyl α-(dimethylphosphono)propionate, 26530-60-9; 2,3-dimethyl-1,4-butadiene, 513-81-5; methyl 3-bromopropionate, 3395-91-3; maleic anhydride, 108-31-6; (methoxymethyl)triphenylphosphonium, 4009-98-7; 1,4-dibromobutane, 110-52-1; diphenyl diselenide, 1666-13-3; methyl 3-(phenylseleno)propionate, 67813-05-2; (*E,E*)-octa-4,6-dienol, 80106-30-5; phenyl selenocyanate, 2179-79-5.

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Olefins from Crowded Carbonyl Compounds with *tert*-Butyllithium (*tert*-Butylmagnesium Chloride)/Thionyl Chloride. Study of Carbocationic Reaction Intermediates and Rearrangement–Cleavage under Stable Ion Conditions Using ^{13}C NMR Spectroscopy[1]

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Crowded carbonyl compounds when reacted with *tert*-butyllithium or *tert*-butylmagnesium chloride followed by thionyl chloride treatment give in a one-pot reaction olefins in good to excellent yields. In the case of highly crowded tertiary systems the reaction occurs either by rearrangement followed by the loss of a *tert*-butyl group (as isobutylene) or rearrangement accompanied by deprotonation, indicating the carbocationic nature of the process. The nature of intermediate carbocations and their cleavage–rearrangement process was probed in SbF_5/SO_2ClF solution of the corresponding alcohols under stable ion conditions using ^{13}C NMR spectroscopy.

Introduction

In the study of the dehydration of di-*tert*-butylmethyl alcohol to give trimethylethylene through elimination of a *tert*-butyl group (as isobutylene), Whitmore and Stahly[2a] established the common basis for intramolecular carbocationic rearrangements. Subsequently, in the solvolysis of (tri-*tert*-butylmethyl)-*p*-nitrobenzoate in a hydroxylic solvent under neutral conditions, Bartlett and Stiles[3]

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