Articles

A New Tied-Back Approach toward the Synthesis of Tetra-*tert*-butylethylene

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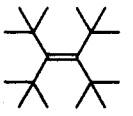
The extremely hindered selenadiazoline 1,1″,5,5″-tetramethyldispiro[3,7-dithiabicyclo[3.3.1]nonane-9,2′-Δ^3-1′,3′,4′-selenadiazoline-5′,9″-3″,7″-dithiabicyclo[3.3.1]nonane] (6) has been prepared as a precursor to bis(1,5-dimethyl-3,7-dithiabicyclo[3.3.1]non-9-ylidene) (8), a "tied-back" analogue of tetra-*tert*-butylethylene (1). The pyrolysis of 6 yields retrocyclization and decomposition products and no 8, presumably due to strain limitations. The ketone 1,5-dimethyl-3,7-dithiabicyclo[3.3.1]nonan-9-one (4) is unreactive toward McMurry coupling to 8.

In the field of strained alkenes, tetra-*tert*-butylethylene (1) has been the ultimate synthetic goal to many workers.[1-16] However, this congested alkene, with its calculated strain energy of between 375–429 kJ/mol and expected double bond torsion of 44–45.5°,[17-20] has remained elusive for the past 18 years.

Although so far unsuccessful, the quest for 1 has seen the synthesis of many alkenes of previously incomprehensible strain.

The most generally applicable procedure for the synthesis of highly strained alkenes has been the thermal 2-fold extrusion of nitrogen and selenium or nitrogen and sulfur from a selenadiazoline[2,21] or thiadiazoline,[1] respectively. However, these routes have their limitations. Neither procedure afforded 1 directly, and the extremely hindered "tied-back" selenadiazolines 2[22] and 3[23] were only stable at low temperatures. No alkenes were afforded upon heating.



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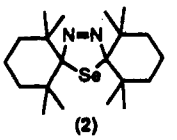

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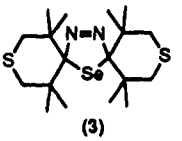

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Guziec *et al.*[7,9,14] via selenadiazolines and Krebs *et al.*[7,13,15,23] via thiadiazolines have successfully prepared several tied-back analogues of 1, with the view of releasing the tie once the central alkene bond has been formed. However, these routes failed as later intermediates underwent strain-relieving side reactions.

Like our predecessors, we viewed a successful synthesis of 1 as involving a tied-back olefinic precursor, prepared via the corresponding selenadiazoline. The untying of this alkene precursor via mild, specific conditions would require intermediates of lower strain energy than 1 and be free of

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(2) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2079.
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(7) Krebs, A.; Rueger, W.; Nickel, W.-U. *Tetrahedron Lett.* **1981**, *22*, 4937.
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(10) Kalinowski, H.-O.; Rocker, E.; Maier, G. *Org. Magn. Res.* **1983**, *21*, 64.
(11) Krebs, A.; Born, W.; Kaletta, B.; Nickel, W.-U.; Rueger, W. *Tetrahedron Lett.* **1983**, *24*, 4821.
(12) Loerzer, T.; Gerke, R.; Luettke, W. *Tetrahedron Lett.* **1983**, *24*, 5861.
(13) Krebs, A.; Nickel, W.-U.; Tikwe, L.; Kopf, J. *Tetrahedron Lett.* **1985**, *26*, 1639.
(14) Cullen, E. R.; Guziec, F. S. *J. Org. Chem.* **1986**, *51*, 1212.
(15) Krebs, A.; Kaletta, B.; Nickel, W.-U.; Rueger, W.; Tikwe, L. *Tetrahedron* **1986**, *42*, 1693.
(16) Garratt, P. J.; Payne, D.; Tocher, D. A. *J. Org. Chem.* **1990**, *55*, 1909.
(17) Lenoir, D.; Dauner, H.; Frank, R. M. *Chem. Ber.* **1980**, *113*, 2636.
(18) Burkert, U. *Tetrahedron* **1981**, *37*, 333.
(19) Krebs, A.; Rueger, W.; Nickel, W.-U.; Wilke, M.; Burkert, U. *Chem. Ber.* **1984**, *117*, 310.
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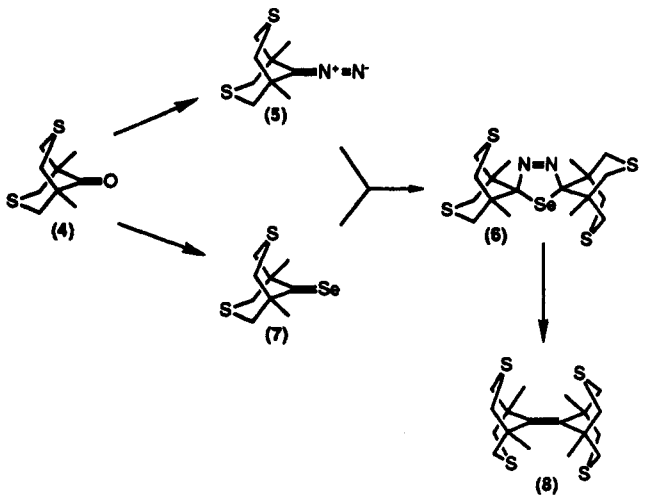
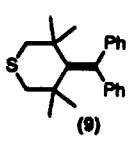
Scheme I



side reactions leading to strain relief. To this end, in the main thrust toward 1, we undertook a synthesis of the selenadiazoline 6, which in turn was to be prepared from the diazoalkane 5 and selone 7. Compounds 5 and 7 are derived from the precursor ketone 4 which is a new tied-back di-*tert*-butyl ketone equivalent.

Selenadiazoline 6, being doubly tied-back, halves the number of methyl groups in steric conflict across the evolving double bond of 8. It is known that the dipole–dipole repulsion and potential overlap of lone electron pairs from sulfur in 3,7-dithiabicyclo[3.3.1]nonanes destabilizes the double-chair arrangement to the point where the boat–chair arrangement is the lowest energy conformer.[24,25] In this conformation the remaining methyl groups of 8 would be in gross conflict. Fortunately, a process exists that relieves this interaction without effecting torsion of the alkene bond. Assisted by the 3,7-dithia interaction, the twin-twist–boat conformation[26,27] is expected to be accessible during the pyrolysis of 6. In this conformation, 8 has the potential to overcome some of the steric crowding between its four methyl groups. Adoption of this conformation in 8 results in one methyl group moving above and the other methyl group moving below the plane of the double bond. Both bicyclic rings are expected to twist in opposite scenes, reducing nonbonded interactions between opposing methyl groups.

The planned selective reduction of 8 to 1 with Raney nickel follows the precedent set by 9[4] and 10.[15] The overall strategy is shown in Scheme I.



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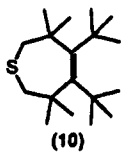
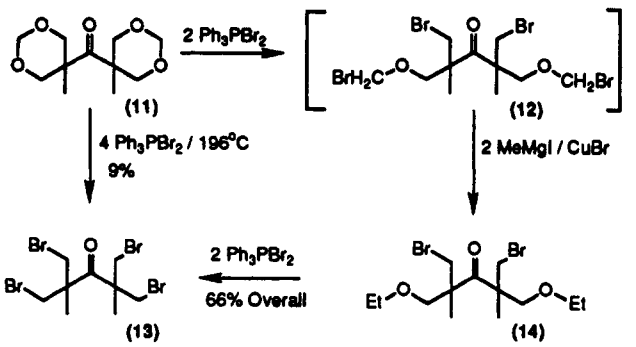


(10)

Less probable, though worthwhile, attempts toward 1, involved the McMurry coupling of the ketone 4.

The starting point of this synthesis is the bis-1,3-dioxane 11, prepared via the literature procedure.[28] Initially, 11 was treated as a tetraether in the conversion to the tetrabromide 13. Refluxing 11 with excess Ph_3PBr_2 in chlorobenzene resulted in a stable product whose ^1H NMR spectrum in the reaction mix was consistent with the bis(bromomethyl ether) 12. This product was extremely reactive toward hydrolysis, complicating its isolation, while in C_6H_5CN solvent the same reaction afforded only 9% of the desired tetrabromide and extensive decomposition. This difficulty was overcome when the proposed intermediate 12 from 11 and 2 equiv of Ph_3PBr_2 in chlorobenzene was treated with catalytic CuBr and 2 equiv of methylmagnesium iodide in tetrahydrofuran, affording the diether 14. Further treatment of the crude product with 2 equiv of Ph_3PBr_2 afforded 13 in 66% overall yield. The diether 14 was readily isolable if required as a mixture of diastereoisomers.



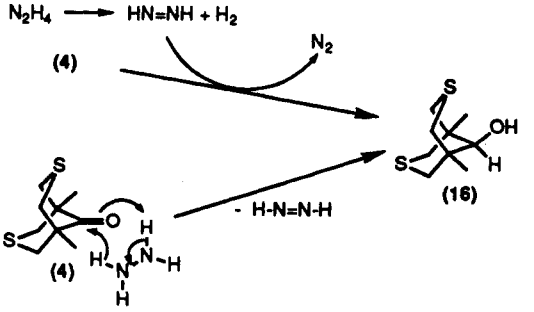
Biscyclization of 13 in dimethylformamide with sodium sulfide afforded the ketone 4 in a pleasing 37% yield from a noxious reaction mixture.

The McMurry coupling of ketone 4 to alkene 8 was attempted following the procedure reported for the preparation of 15.[29] The ketone 4 was refluxed with a

(15)

titanium suspension (prepared from $TiCl_3$ and $LiAlH_4$) in tetrahydrofuran for 48 h. Only ketone 4 and no coupled or reduced products were detected from the reaction. We believe the bicyclic ring structure has not sufficiently reduced the steric hindrance around the ketone function in this reaction.

Scheme II



(24) Zefirov, N. S.; Rogozina, S. V. *Tetrahedron* **1974**, *30*, 2345.
(25) Gleiter, R.; Kobayashi, M.; Zefirov, N. S.; Palyulin, J. A. *Doklady Chem.* (Engl. Transl.) **1977**, *235*, 396.
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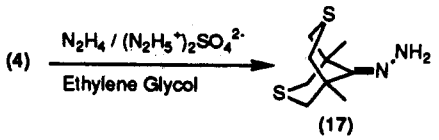
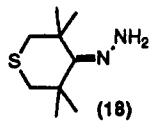
(27) Bishop, R.; Craig, D. C.; Scudder, M. L. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1473.
(28) Wollner, J.; Engelhardt, F. *Chem. Ber.* **1962**, *95*, 30.
(29) Bohrer, G.; Knorr, R. *Tetrahedron Lett.* **1984**, *25*, 3675.

Conversion of 4 to the hydrazone 17 was expected to be a trivial task. However, 4 mimicked the inert behavior of di-*tert*-butyl ketone[30] and dimesityl ketone[31] to anhydrous hydrazine. Attempting to promote the reaction by passing the refluxing vapors over 3-Å molecular sieves or using catalytic amounts of either hydroxide or acid simply afforded only the reduced alcohol 16. Either of the pathways in Scheme II may be invoked to account for this result. This alcohol was also unequivocally prepared by the reduction of 4 with lithium aluminum hydride. The formation of the alcohol in preference to 17 is believed to



(17)

be a consequence of the steric hindrance to S_N2 attack of the hydrazine nitrogen on the carbonyl. Clearly, 4 is hindered, particularly if the bicyclic system adopts a conformation other than the double chair. However, in the light of the successful preparation of 18 in 74% yield by standard procedures,[4] this result was unexpected.

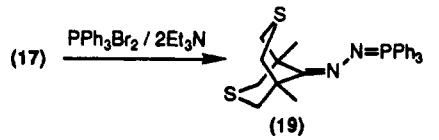


(18)

The successful preparation of 17 was achieved in the presence of hydrazinium sulfate and anhydrous hydrazine in ethylene glycol. This new hydrazone was fully characterized with all spectroscopic techniques employed being consistent with the assignment.

Both the ^1H and ^{13}C NMR spectra display only two types of methylene resonances which are unchanged within the temperature range −60 to +55 °C. This implies that 17 is not fixed in the boat–chair conformation; a double chair, twin-twist–boat or rapid equilibrium between conformers is therefore implied.

Historically, the most widely employed method for preparing hindered diazoalkanes has been the preparation of the (triphenylphosphoranylidene)hydrazone from the hydrazone, followed by vacuum pyrolysis.[2,22,23] Diazoalkanes are afforded in typically moderate to good yields. (Triphenylphosphoranylidene)hydrazone 19 was prepared



(19)

by the standard procedure in 86% yield. The X-ray crystal structure of this compound is displayed in Figures 1 and 2. The determination revealed that in the solid state the lowest energy conformation is the boat–chair arrangement previously discussed. A close N(1)–C(8) contact (2.626 Å) is observed while the N(2) lone pair is oriented toward the C(9) methyl group. This congestion, centered around C(1), is invoked to explain the out-of-plane deformations observed. This ability of the bicyclic system to reduce steric congestion by conformational change is heartening as a similar process was anticipated in the alkene 8.

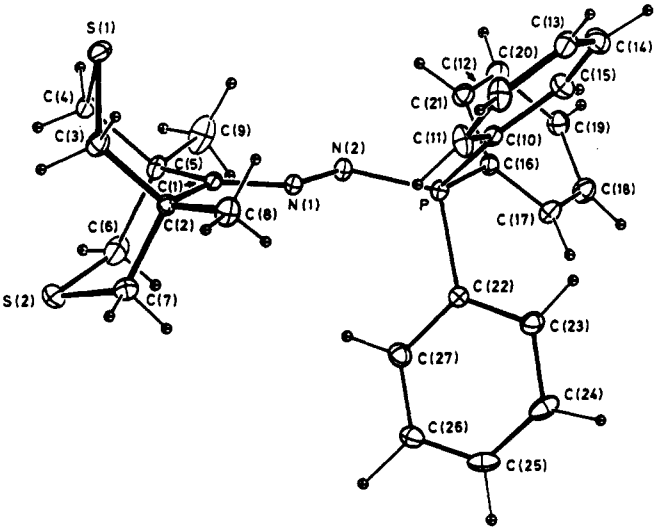


Figure 1. Crystal structure of 19 showing the crystallographic numbering system used.

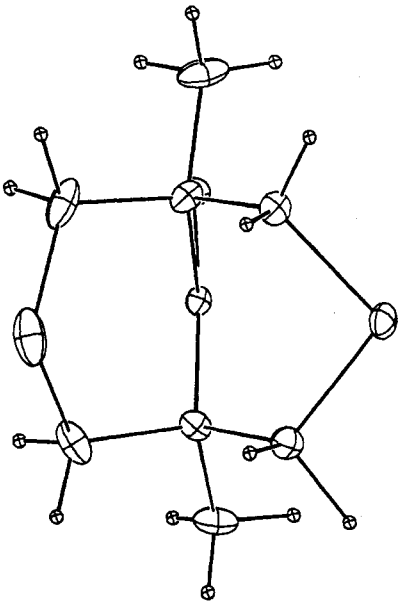


Figure 2. Crystal structure of only the dithiabicyclononane part of 19 viewed from the opposite side to the (omitted) triphenylphosphoranylidene group.

The forced interaction of the C(9) methyl with the N(2) lone pair results in a δ 2.16 ppm methyl resonance in the ^1H NMR spectrum (Figure 3). A phosphorus to C(9) hydrogen coupling of 2.4 Hz is observed. The ^{13}C NMR spectrum indicates that this may arise via the C(9)–N(2) lone pair interaction as this spectrum displayed a phosphorus to C(1) coupling of 37.2 Hz and a 3.0 Hz coupling to C(9). These doublets collapse to singlets upon phosphorus irradiation. No couplings of phosphorus to C(2), C(5), or C(8) were observed. There is, however, insufficient evidence to rule out the through-bond coupling mechanism to the C(9) carbon and hydrogen.

The C(3) and C(7) methylene resonances in the ^1H NMR spectrum are observed as two doublets while the C(4) and C(6) resonances appear as a singlet which only splits into an AB system below −30 °C.

The equivalence of the C(3) and C(7) methylenes (−60 to +27 °C) and the coalescence of the C(4),C(6) hydrogens

(30) Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527.
(31) Fung, N. Y. M. Masters Thesis, University of Western Ontario, 1979.

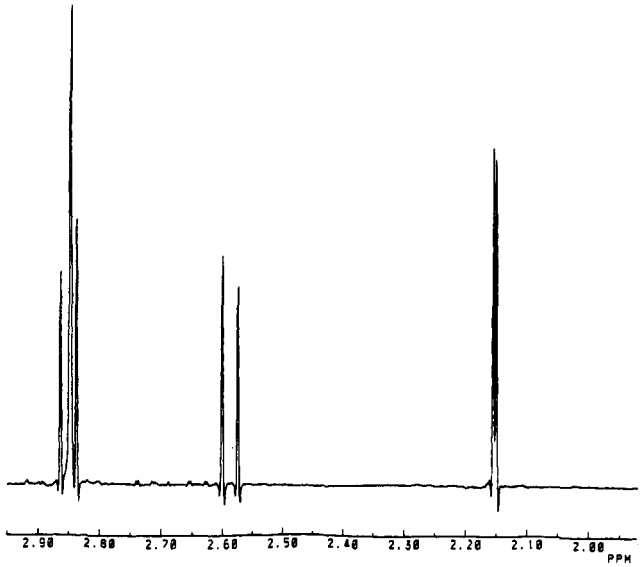


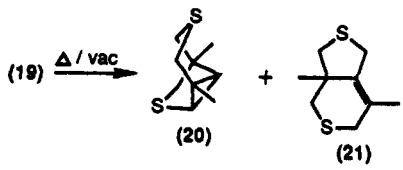
Figure 3. ^{1}H NMR spectrum of **19**, expansion of δ 2.00–2.95 ppm.

at ambient temperatures strongly supports a rapid equilibrium but it appears impossible to distinguish the conformers involved.

The pyrolysis of (triphenylphosphoranylidene)hydrazones with selenium has previously been shown to afford both the diazoalkane and selenone *in situ*, hence affording symmetrical alkenes directly.[2,9]

However, no strained alkene was observed by ^{13}C NMR spectroscopy from the pyrolysis of **19** with excess selenium. From previous work, the quaternary carbons of highly strained alkenes appear in the region 150–155 ppm.[15] It is through this region of the ^{13}C NMR spectrum that reactions were monitored. This route was abandoned in favor of the isolation of **6** prior to pyrolysis.

Approaches toward **5** initially proved unrewarding as the vacuum pyrolysis of **19** at 200 °C/0.4 mmHg afforded a clear oil containing no diazoalkane by visual observation or infrared spectroscopy. From this oil were isolated the two major components which were identified by spectroscopic techniques as the carbene rearrangement products **20** and **21**.

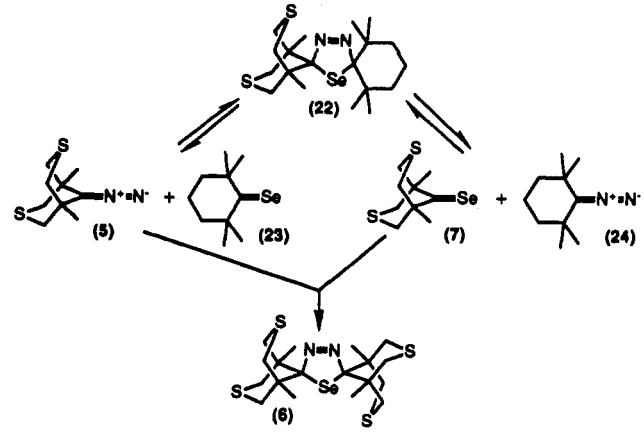


The cyclopropyl ring compound **20** arises via a carbene insertion into a methylene C–H bond. This structure is assigned primarily on its ^{1}H NMR spectrum. The ^{13}C NMR spectra is consistent with the structure, though one quaternary carbon was unobserved.

The bicyclic alkene **21** arises from a 1,2-alkyl shift with formation of a new double bond. All the spectroscopic data were consistent with this structure.

An alternate preparation of diazoalkanes, developed by Guziec *et al.*,[22] proved successful. The direct oxidation of the hydrazone **17** with barium manganate/calcium oxide in dichloromethane proceeded in near-qualitative yield. For further elaboration, the reaction mixture required no more than filtering, evaporation then taking up the diazoalkane **5** in hexane. This diazoalkane was moderately

Scheme III



stable at ambient temperatures but was generally prepared as required.

$$\mathbf{17} \xrightarrow{BaMnO_4 + CaO} \mathbf{5}$$

The selone **7** was prepared via a modification of the general procedure reported by Barton.[2,21] A solution of **19** was evaporated onto a large excess of fresh selenium powder and the mixture pyrolyzed under vacuum to yield a deep green oil from which was obtained the selone in 20% yield.

This selone is green in solution or as an oil but reversibly forms red-brown crystals. That the compound is the first known hindered selone not to be blue is surprising. The visible–ultraviolet spectrum of **7** in dichloromethane [λ_{max} 674 nm (ϵ = 87), 305 nm (ϵ = 12 500), 256 nm (ϵ = 20 100)] displays a stronger bathochromic shifted absorbance in the near-ultraviolet compared to the blue selones. The visible-ultraviolet spectrum of di-*tert*-butyl selone, for example, displays λ_{max} 710 nm (ϵ = 21), 268 nm (ϵ = 7200), 230 nm (ϵ = 2800).

The X-ray structure of **7** displayed no unusual structural features.[32] The C=Se bond length was 1.774 Å, and the bicyclo[3.3.1]nonane system was in a double-chair conformation. Both the ^{1}H and ^{13}C NMR spectra of **4** and **7** display equivalent methylenes in solution at ambient temperatures. This supports a rapid equilibrium between conformers.

The stability of **7** is also remarkable. Blue selones, including our experiences with fenchone selone and 2,2,6,6-tetramethylcyclohexaneselone **23**, are reported to be thermally stable but undergo rapid aerial oxidation in the presence of light. Crystals of **7** displayed no signs of degradation upon prolonged standing.

In the meantime, a far more economical *in situ* generation of **7** was developed. It is known that the retrocyclization of hindered unsymmetrical selenadiazolines yields both the starting reagents and the products of exchanged seleno and diazo functions. On the basis of this observation, the selenadiazoline **22** was prepared from the available diazoalkane **5** and the selone **23**. Retrocyclization of **22** could, in principle, yield **7** and hence the selenadioazoline **6** (see Scheme III).

To this end, the reaction of **23**, prepared via a modification upon Guziec's procedure,[33] with 2 equiv of the diazoalkane **5** in hexane rapidly yielded **6** as a crystalline

(32) Brooks, P. R.; Counter, J. A.; Bishop, R.; Tiekink, E. R. T. *Acta Crystallogr., Sect. C* **1991**, *47*, 1939.
(33) Guziec, F. S.; Moustakis, C. A. *J. Org. Chem.* **1984**, *49*, 189.

solid in 73% yield based upon the hydrazone 17. This result indicates that the labile selenadiazoline 22 was retrocyclizing to yield the least hindered selone 7, from which the insoluble 6 was forming. It can therefore be concluded that the steric hindrance is less in 6 than in 3 or 22.

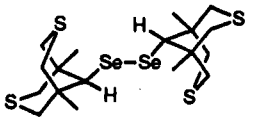
This selenadiazoline was thermally stable up to its melting point of 156 °C, a result that contrasts significantly with the instability of 2 and 3. These results support our initial hypothesis of the nature and function of the bicyclic rings.

A successful alkene synthesis was still far from assured as an 8% w/w solution of 6 in $CDCl_3$ displayed 18% retrocyclization at 20 °C. The retrocyclization of 6 followed by decomposition of 5 may predominate at elevated temperatures.

In general, hindered selenodiazolines are heated neat to above their melting points for 12–24 h to effect nitrogen and selenium extrusion.[22,23] Guziec has demonstrated that these reactions are significantly advanced in 2 min at 190 °C.[22] The prolonged heating afforded only minor increases in the yields of the alkenes which were stable under the conditions.

The pyrolysis of 6 was optimized at 160 °C for 12 min via examination of the crude reaction products by ^{13}C NMR. This revealed strong, complex aliphatic resonances and weak resonances at 153.7, 154.4, and 155.1 ppm. These resonances disappeared at higher temperatures or longer reaction times. Even after allowing for variations in sensitivity, the intensity of these signals indicated that 8, if responsible for one of the resonances, represented less than 2% of the mixture.

The crude product from the pyrolysis of 6 was an amorphous orange solid. From this, partial recovery of the selone 7 and diselenide 25 was achieved by vacuum



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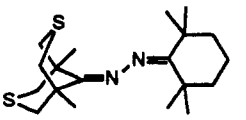
distillation and recrystallization, respectively. Other than these organoseleniums, no other products were obtained in reasonable purity by distillation, recrystallization, or chromatography. Furthermore, hazards associated with organoseleniums and the need to examine all fractions by ^{13}C NMR compounded these difficulties. Our attempts to obtain the product giving rise to the most intense peak in the expected region of the ^{13}C NMR spectrum (154.4 ppm) were frustrated by continual contamination. Particularly evident were organoseleniums. The decomposition of the remaining organoseleniums was achieved by the reaction with sodium borohydride in MeOH/THF. Elution of the concentrates off silica afforded a cleaner product. Further separation via a chromatotron gave the crystalline compound giving rise to the absorbance at 154.4 ppm in the ^{13}C NMR spectrum.

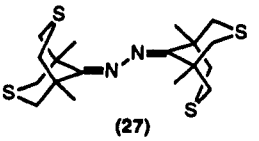
This compound is the unsymmetrical azine 26. Formation of 26 presumably is a consequence of incomplete formation of 6 from 22. Even so, the available spectroscopic evidence was consistent with 6 being free of impurity. It can therefore be assumed that 26 is formed in high yield from 22 contaminating 6. Retrocyclization of 22 yields 7 and diazo-2,2,6,6-tetramethylcyclohexane 24. The selone 7 and diazoalkane 5 are generated from



(26)

retrocyclization of 6. Loss of N_2 from 24 yields a carbene which couples with 5, yielding 26. Guziec has previously shown that 24 is relatively unstable, decomposing to the carbene (half-life at 126 °C of 9 min).[34]

In comparison, the ^{13}C NMR spectra of the crude reaction mixture indicated that the symmetrical azine 27 [prepared via an alternate route] gave rise to the resonance at 153.7 ppm and was present in smaller quantities than 26. This suggests a low-yielding coupling of 5 and the carbene derived from 5.



(27)

Although the compound giving rise to the resonance at 155.1 ppm in the ^{13}C NMR spectrum could not be isolated, this, if 8, was never present in more than trace quantities. The 3,7-dithiabicyclo[3.3.1]nonane system has not sufficiently reduced steric conflict in 6 to allow progressive loss of N_2 and Se to compete with retrocyclization and decomposition.

The bicyclic system is a major improvement compared with the mono tied-back selenadiazolines 2 and 3. The thermal stability of 6 indicates that the strain in 8 is not far above the limits of this procedure.

Alternate pathways to 8, such as dimeric coupling of the carbene derived from 5, are currently underway.

Experimental Section

Infrared spectra (IR) were recorded on a Hitachi 260-10 instrument. Melting points (mp) were recorded on a Kofler hot stage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-500 at 500 and 126 MHz, respectively, and are reported relative to tetramethylsilane reference. Mass spectra were recorded on an A.E.I. MS-12 instrument at 70 eV or via chemical ionization on a V.G. MM-16F instrument (VG, CI). High-resolution mass spectrometry was performed on a Bruker CMS 47 FTICR instrument. Visible–ultraviolet spectra were obtained on a Hitachi U-3200 spectrophotometer.

2,4-Bis(bromomethyl)-1,5-dibromo-2,4-dimethylpentan-3-one (13). The bis-1,3-dioxane[28] 11 (83 g, 0.36 mol) and Ph_3P (208 g, 0.79 mol) were dissolved in chlorobenzene (500 mL) and deoxygenated under N_2. Bromine (122 g, 0.76 mol) was slowly injected followed by a 16-h reflux. To this was added THF (650 mL) and the solution cooled in ice. Cuprous bromide (104 g, 72 mmol) was added followed by titration with MeMgI (0.8 mol) in Et_2O (600 mL), the end point being indicated by an orange/brown to gray color change. The THF was removed under reduced pressure, and the residue was cooled. Filtration of the solution and washing with hexane removed Ph_3PO. The filtrate was concentrated and added to Ph_3PBr_2 (2.2 equiv) in chlorobenzene (500 mL) under N_2. This was refluxed for 15 h. The dark mixture was washed with H_2O (400 mL), filtered, separated, and evaporated to give a black tar. This was dissolved in hot CH_2Cl_2 (300 mL), diluted with hexane (600 mL), cooled, and

(34) Guziec, F. S.; SanFilippo, L. J.; Murphy, C. J.; Moustakis, C. A.; Cullen, E. R. *Tetrahedron* **1985**, *41*, 4843.

(35) Dance, I. G.; Guerney, P. J.; Rae, A. D.; Scudder, M. L. *Inorg. Chem.* **1983**, *22*, 2883.

decanted. This residue was further extracted with hot hexane (2 × 500 mL) and the extracts were combined. Evaporation yielded the crude product which was further purified on a silica column with hexane/ethyl acetate. Yield: 108 g, 66%. Mp: 52–5 °C. Found: C, 24.03; H, 3.24. $C_9H_{14}Br_4O$ requires: C, 23.61; H, 3.08. IR (paraffin mull): 1698, 1414, 1255, 988, 808 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 3.78 (s, 8H); 1.60 (s, 6H). ^{13}C NMR ($CDCl_3$) δ: 205.6 (C); 54.8 (C); 38.9 (CH_2); 21.3 (CH_3). MS m/z^+ (70 eV): 379 (M − Br, 1); 377 (M − Br, 1); 245 (31); 243 (62); 241 (33); 217 (50); 215 (100); 213 (52); 135 (67); 133 (69%).

1,5-Dimethyl-3,7-dithiabicyclo[3.3.1]nonan-9-one (4). A solution of the tetrabromide **13** (15.85 g, 35.8 mmol) and $Na_2S·9H_2O$ (45 g, 187 mmol) in DMF (160 mL) was refluxed under Ar for 45 min. The cooled solution was diluted with H_2O (500 mL) and extracted with Et_2O (3 × 30 mL). The combined organic extracts were backwashed with H_2O and then with brine and dried. Evaporation gave a foul smelling oil (5.1 g). Elution of this oil through alumina with hexane/Et_2O and recrystallization afforded **4** (2.67 g, 37%). Mp 66–7 °C. Found: C, 53.69; H, 7.25; S, 31.80. $C_9H_{14}OS_2$ requires C, 53.42; H, 6.96; S, 31.69. IR (paraffin mull): 1703, 1410, 1304, 1122, 998, 895 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 3.24 (d, J = 13.7 Hz, 4H); 2.70 (d, J = 13.7 Hz, 4H); 1.23 (s, 6H). ^{13}C NMR ($CDCl_3$) δ: 212.7 (C); 49.2 (C); 41.7 (CH_2); 24.8 (CH_3). MS m/z^+ (GC–MS, OV-1): 204 (11); 202 (100); 155 (21); 141 (10); 133 (8); 119 (33); 109 (20); 87 (47).

1,5-Dimethyl-3,7-dithiabicyclo[3.3.1]nonan-9-ol (16). The alcohol **16** was unambiguously prepared by reduction of the ketone **4**.

To a stirred suspension of $LiAlH_4$ (0.05 g, 1.3 mmol) in THF (2 mL) was added the ketone **4** (100 mg, 0.50 mmol). After the suspension was stirred overnight, the excess hydride was destroyed with EtOAc. Water (10 mL) was added and then the solution filtered and the residue washed with Et_2O (3 mL). The filtrate was extracted with more Et_2O (3 mL), and the combined organic extracts were washed with brine and dried. Evaporation and recrystallization from EtOAc/hexane afforded the alcohol **16** (82 mg, 81%) identical by infrared and ^{1}H NMR (500 MHz) to that prepared via hydrazine reduction. Mp: 194 °C. IR (paraffin mull): 3340, 1268, 1100, 1053, 900, 848 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 3.10 (d, J = 9.9 Hz, 1H, collapses to a singlet on D_2O exchange); 3.05 (d, J = 9.9 Hz, 1H, exchangeable with D_2O); 2.93 (d, J = 13.8 Hz, 2H); 2.66 (d, J = 14.0 Hz, 2H); 2.57 (d, J = 13.8 Hz, 2H); 2.47 (d, J = 14.0 Hz, 2H); 1.23 (s, 6H). ^{13}C NMR ($CDCl_3$) δ: 80.9 (CH); 41.5 (CH_2); 35.6 (C); 32.7 (CH_2); 28.5 (CH_3). MS m/z^+ (70 eV): 206 (10); 204 (100); 149 (6); 139 (6); 125 (13); 109 (11); 99 (27); 87 (36).

1,5-Dimethyl-3,7-dithiabicyclo[3.3.1]nonan-9-one hydrazone (17). A solution of ketone **4** (0.72 g, 3.56 mmol), hydrazinium sulfate (0.38 g, 2.9 mmol), and anhydrous hydrazine (5.2 g, 162 mmol) in dry ethylene glycol (10 mL) was refluxed under Ar for 11 h. The cooled solution was diluted with H_2O (50 mL) and extracted with Et_2O (2 × 15 mL). The combined organic extracts were washed with H_2O (10 mL) and then with brine, dried, and evaporated. Recrystallization from hexane yielded **17** (0.568 g, 74%). Mp: 124–7 °C. M^+ found 216.07523; calcd for $C_9H_{16}N_2S_2$ 216.07494. IR (paraffin mull): 3395, 3340, 3245, 1655, 1610, 1423, 1043, 842 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 5.54 (broad s, 2H); 2.89 (pseudo t, J = 12.0 Hz, 4H); 2.72 (dd, J = 1.9 and 13.3 Hz, 2H); 2.63 (dd, J = 1.9 and 13.3 Hz, 2H); 1.79 (s, 3H); 1.20 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 150.9 (C); 45.5 (C); 43.6 (C); 41.4 (CH_2); 41.0 (CH_2); 30.6 (CH_3), 29.8 (CH_3). MS m/z^+ (70 eV): 218 (10); 217 (12); 216 (100); 203 (3); 202 (4); 200 (4); 183 (8).

1,5-Dimethyl-3,7-dithiabicyclo[3.3.1]nonan-9-one (Triphenylphosphoranylidene)hydrazone (19). To a solution of Ph_3P (0.54 g, 2.06 mmol) in dry benzene (10 mL) under Ar was added Br_2 (0.33 g, 2.06 mmol) in benzene (10 mL). After 30 min, the hydrazone **17** (0.448 g, 2.07 mmol) was added, and then Et_3N (0.6 mL, 0.44 g, 4.3 mmol) in benzene (15 mL) was injected into the mixture. The suspension was stirred for 19 h and then filtered and washed with benzene. The filtrate was evaporated to afford a yellow solid. Recrystallization from CH_2Cl_2/hexane gave **19** (0.85 g, 86%). Mp dec: 187–9 °C. Found: C, 67.90; H, 6.01; N, 5.87; S, 13.97. $C_{27}H_{29}N_2PS_2$ requires: C, 68.03; H, 6.13; N, 5.87; S, 13.45. IR (paraffin mull): 3065, 1590, 1570, 1120, 1110, 1058, 1030, 1000, 965, 815, 745, 725, 715, 692 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 7.70 (dd, J = 7.4 and 11.0 Hz, 6H); 7.55–7.46 (complex m, 3H); 7.44 (td, J = 2.7 and 7.7 Hz, 6H); 2.85 (s, 4H); 2.85 (d, J = 13.1 Hz, 2H); 2.59 (d, J = 13.1 Hz, 2H); 2.16 (d, J = 2.4 Hz, 3H); 1.01 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 153.0 (d, J = 37.2 Hz, C); 133.1 (d, J = 8.0 Hz, CH); 131.4 (CH); 130.2 (d, J = 92.2 Hz, C); 128.2 (d, J = 11.3 Hz, CH); 44.2 (C); 43.5 (C); 41.7 (CH_2); 41.2 (CH_2); 32.3 (d, J = 3.0 Hz, CH_3), 30.2 (CH_3).

Attempted Preparation of 9-Diazo-1,5-dimethyl-3,7-dithiabicyclo[3.3.1] nonane (5). Method A. The (triphenylphosphoranylidene)hydrazone **19** (39 mg, 0.082 mmol) was heated to its melting point at 0.4 mmHg with a collection of volatile decomposition products at −78 °C. A clear oil (14 mg) was slowly collected in the cold trap. No pink diazo color was observed, and the infrared spectrum did not contain the characteristic diazo peak at 2000–2100 cm^{-1}. Elution of this oil through alumina with hexane/Et_2O afforded **20** (2.1 mg, 14%) and **21** (4.3 mg, 28%).

1,5-Dimethyl-3,7-dithiatricyclo[3.3.1.0^{2,9}]nonane (20). ^{1}H NMR ($CDCl_3$) δ: 3.08 (d, J = 14.0 Hz, 1H); 2.99 (d, J = 11.6 Hz, 1H); 2.89 (d, J = 11.6 Hz, 1H); 2.70 (d, J = 11.8 Hz, 1H); 2.62 (d, J = 11.8 Hz, 1H); 2.52 (d, J = 14.0 Hz, 1H); 2.40 (d, J = 7.3 Hz, 1H); 1.37 (s, 3H); 1.24 (d, J = 7.3 Hz, 1H), 1.17 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 50.4 (CH_2); 40.2 (CH); 36.8 (CH); 35.1 (C), 30.2 (CH_3); 29.7 (CH_2); 26.2 (CH_2), 24.8 (CH_3). One further quaternary carbon not observed.

2,6-Dimethyl-4,8-dithiabicyclo[4.3.0]non-1-ene (21). Mp: 37–8 °C. IR (neat): 2940, 1453, 1365, 1264, 1224, 1200, 1098, 940, 915, 741, 715 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 3.71 (d, J = 14.0 Hz, 1H); 3.49 (d, J = 14.0 Hz, 1H); 3.25 (d, J = 17.1 Hz, 1H); 2.77 (d, J = 17.1 Hz, 1H); 2.67 (s, 2H); 2.62 (d, J = 13.0 Hz, 1H); 2.59 (d, J = 13.0 Hz, 1H); 1.72 (s, 3H); 1.36 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 137.4 (C); 123.4 (C); 44.5 (CH_2); 43.3 (C); 37.3 (CH_2); 33.0 (CH_2); 30.5 (CH_2); 24.7 (CH_3); 20.7 (CH_3).

9-Diazo-1,5-dimethyl-3,7-dithiabicyclo[3.3.1]-nonane (5). Method B. To an oven-dried and cooled mixture of CaO (1.0 g) and sand (1.1 g) was added $BaMnO_4$ (1.44 g, 5.6 mmol). The hydrazone **17** (0.72 g, 3.33 mmol) in dry CH_2Cl_2 (10 mL) was added and the slurry stirred for 1 h. The slurry was filtered and evaporated to give a pink oil whose ^{1}H NMR (60 MHz) spectrum indicated a quantitative conversion. This product was used without further purification. IR (neat): 2060, 1290, 1230, 1145, 1118, 966, 741 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.73 (d, J = 13.3 Hz, 4H); 2.65 (d, J = 13.3 Hz, 4H); 1.24 (s, 6H).

1,5-Dimethyl-3,7-dithiabicyclo[3.3.1]nonane-9-selone (7). To a solution of the (triphenylphosphoranylidene)hydrazone **19** (110 mg, 0.231 mmol) in CH_2Cl_2 was added freshly powdered selenium (1.2 g, 1.5 mmol), and then the solvent was evaporated. This mixture was then heated to 200 °C/0.2 mmHg with a collection of volatile materials at −78 °C. A green liquid and some colorless solid were collected. The liquid was distilled off the solid. Preparative TLC on dried silica developing with benzene afforded the selone **7** (R_f = 0.83) as a stable green oil (12 mg, 20%). This oil reversibly crystallizes to a red-brown solid. Mp: 84–6 °C. IR (paraffin mull): 1410, 1370, 1307, 1275, 1160, 1115, 1020, 920, 820 cm^{-1}. VIS–U V (H_2CCl_2): 674 nm (ε = 87); 305 nm (ε = 12 500); 256 nm (ε = 20 100). ^{1}H NMR ($CDCl_3$) δ: 3.22 (d, J = 13.5 Hz, 4H); 2.90 (d, J = 13.5 Hz, 4H); 1.76 (s, 6H). ^{13}C NMR ($CDCl_3$) δ: 279.2 (C); 62.7 (C); 42.5 (CH_2); 36.2 (CH_3). MS m/z^+ (VG, CI, NH_4^+): 269 (28); 268 (13); 267 (100); 266 (14); 265 (51); 264 (22); 263 (19); 219 (7); 202 (4); 189 (3); 183 (3).

2,2,6,6-Tetramethylcyclohexaneselone (23). A solution of 2,2,6,6-tetramethylcyclohexanone hydrazone[23] (1.1 g, 6.54 mmol) and Et_3N (1.4 g, 13.9 mmol) in CH_2Cl_2 (50 mL) was added over 2 h to selenium monobromide (2.5 g, 7.81 mmol) in CH_2Cl_2 (250 mL) under Ar at −78 °C. The solution was warmed to room temperature over 20 min and then filtered. The filtrate was washed with water and then filtered through anhydrous K_2CO_3 (10 g) and Na_2SO_4 (5 g). Evaporation afforded a green oil. The oil was Kugelrohr distilled at 80 °C/1 mmHg. The distillate was warmed to 70 °C under Ar and then redistilled at 1 mmHg to give the blue selone as a low-melting solid (0.8 g, 56%). IR (neat): 1463, 1383, 1360, 1063, 1030, 985, 735 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.86–1.77 (comp. m, 6H); 1.41 (s, 12H).

1,1″,5,5″-Tetramethyldispiro[3,7-dithiabicyclo[3.3.1]-nonane-9,2′-Δ^3-1′,3′,4′-selenadiazoline-5′,9″-3″,7″-dithiabicyclo[3.3.1]nonane (6). To a solution of the diazoalkane **5**, prepared from **17** (0.72 g, 3.33 mmol), in CH_2Cl_2/hexane

(1:3, 40 mL) was added selone **23** (0.40 g, 1.84 mmol). The green solution was warmed and scratched whereupon flaky crystals separated. The mixture was cooled in the freezer overnight giving a pink solution and cream crystals. The crystals were filtered, washed with hexane, and dried under vacuum to afford the selenadiazoline **6** (0.58 g, 73%) from the hydrazone **17**. Mp: 156 °C. IR (paraffin mull): 3048, 1555, 1495, 1418, 1298, 1110, 938, 822 cm^{-1}. ^1H NMR (8% solution in $CDCl_3$) δ: 3.93 (d, J = 14.3 Hz, 4H); 3.44 (d, J = 14.0 Hz, 4H); 2.52 (d, J = 14.0 Hz, 4H); 2.30 (d, J = 14.3 Hz, 4H); 1.08 (s, 12H). This spectrum displayed partial retrocyclization affording diazoalkane **5**, selone **7**, and selenadiazoline **6** in a ratio 1:1:4.3. ^{13}C NMR ($CDCl_3$) δ: 121.9 (C); 44.9 (C); 39.3 (CH_2); 38.5 (CH_2); 36.3 (CH_3).

This spectrum also contained signals resulting from retrocyclization.

Attempted Preparation of Bis(1,5-dimethyl-3,7-dithiabicyclo[3.3.1]non-9-ylidene) (8). Method A. To a solution of $TiCl_3$ (0.14 g, 0.91 mmol) in dry THF (2 mL) under Ar at 0 °C was added $LiAlH_4$ (17 mg, 0.45 mmol). A black precipitate readily formed with gas evolution. After 30 min at 0 °C the mixture was refluxed for 1 h and then cooled to 0 °C. The ketone **4** (84 mg, 0.42 mmol) was added, and then the mixture was refluxed under Ar for 48 h. This mixture was cooled, poured onto HCl (2 M, 10 mL), and extracted with CH_2Cl_2. Backwashing the organic extracts with H_2O and then brine followed by drying and evaporation of the solvent afforded a white solid (75 mg). Infrared, GC, and ^{13}C NMR analysis of the product indicated only the starting ketone present and no coupled or reduced products.

Method B. The selenadiazoline **6** (5.6 g, 13.5 mmol) was heated to 160 °C under Ar for 12 min. The solid melted to a green oil with gas evolution and solidified to a glass upon cooling. The volatiles were removed at 110 °C/0.5 mmHg and afforded partial recovery of the selenone **7** (70 mg) upon further workup. The distillation residues were dissolved in CH_2Cl_2 (3 mL) and eluted off silica with hexane/EtOAc. Examination by ^{13}C NMR showed extensive contamination in fractions containing 150–5 ppm resonances. The diselenide **25** (0.12 g, 2%) was recovered by further recrystallization. The fractions displaying suspected product were combined (2.05 g) and treated portionwise in MeOH/THF (1:1, 20 mL) with $NaBH_4$ (0.16 g) under N_2. A rapid color change from green to yellow with gas evolution occured. After 1 h this was evaporated and stirred in Et_2O (15 mL) then the soluble portion eluted off silica with Et_2O. The cleaner product (1.29 g) was further eluted through silica with benzene to afford 270 mg of product. Final purification on a Chromatotron with hexane followed by recrystallization yielded the unsymmetrical azine **26** (45 mg).

Bis(1,5-dimethyl-3,7-dithiabicyclo[3.3.1]non-9-yl) Diselenide (25). Mp: 210–5 °C. IR (paraffin mull): 1412, 1270, 1218, 1155, 895, 755 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.14 (s, 2H); 2.87 (d, J = 13.8 Hz, 4H); 2.67 (d, J = 13.7 Hz, 4H); 2.56 (d, J = 13.7 Hz, 4H); 2.51 (d, J = 13.8 Hz, 4H); 1.47 (s, 12H). ^{13}C NMR ($CDCl_3$) δ: 71.4 (CH); 41.0 (CH_2); 37.4 (C); 34.7 (CH_2); 34.5 (CH_3). MS m/z^+ (VG, CI, NH_4^+): 269 (37); 268 (14); 267 (100); 266 (7); 265 (52); 264 (19); 263 (12); 189 (51); 188 (5); 187 (21).

9-[(2,2,6,6-Tetramethylcyclohexyl)hydrazono]-1,5-dimethyl-3,7-dithiabicyclo[3.3.1]nonane (26). Mp: 103–7 °C. IR (paraffin mull): 1600, 1419, 1379, 1293, 1225, 1110, 1085, 973, 890, 740 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.95 (d, J = 13.4 Hz, 2H); 2.87 (d, J = 13.4Hz, 2H); 2.74 (psuedo triplet, J = 13.0Hz, 4H); 1.61 (m, J = 6.1Hz, 2H); 1.53 (s, 3H); 1.53 (m, J = 6.1Hz, 4H); 1.35 (s, 3H); 1.24 (s, 6H); 1.16 (s, 6H). ^{13}C NMR ($CDCl_3$) δ: 163.9 (C); 154.4 (C); 45.4 (C); 44.3 (C); 41.3 (CH_2); 41.1 (CH_2); 41.0 (CH_2); 39.3 (CH); 38.2 (C); 38.1 (CH_2); 31.4 (CH_3); 29.7 (CH_3); 29.3 (CH_3); 27.1 (CH_3); 17.5 (CH_2). MS m/z^+ (70 eV): 353 (30); 352 (100); 319 (52); 305 (39); 297 (26); 265 (50); 145 (35).

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Supplementary Material Available: X-ray study of **19** (as Tables 1–4) and ^1H NMR spectra of compounds **6**, **7**, **16**, **17**, **20**, **21**, **23**, **25**, and **26** (15 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.