5714 J. Org. Chem. 1995, 60, 5714-5716

Bridgehead-Substituted Bicyclo[3.3.1]nonenes and Their Benzo and Dibenzo Derivatives

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Received March 27, 1995

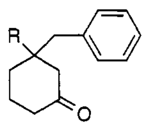
Bridged bicyclic molecules with halogens at bridgehead positions have played key roles in establishing geometrical requirements for formation of carbocations,[1a,b] carbanions,[1a] and free radicals.[1a,c]

Studies of 1-halotriptycenes[2] and other derivatives of 1-halobicyclo[2.2.2]octenes,[1a,b] for instance, have demonstrated the lack of resonance stabilization of carbocations in systems in which adjacent π-bonds are essentially orthogonal to the cationic centers. Less evidence is available, however, as to the extent of resonance stabilization of bridgehead carbocations and other reactive intermediates in larger unsaturated bicyclic systems. This appears to be due to the absence of good methods for the synthesis of such systems.

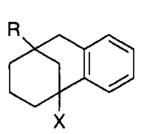
In contrast to the bicyclo[2.2.2]octene series, in which many examples of molecules with bridgehead halogens are known, the literature appears to contain only two reports of the synthesis of 1-halobicyclo[3.3.1]nonene derivatives. In one instance,[3] a small quantity of an equimolar mixture of $\Delta 2$- and $\Delta 3$-1-chlorobicyclo[3.3.1]nonenes was obtained by a procedure starting with bicyclo[3.3.1]non-1-ene, which is itself available only by complex multistep processes.[4] The second procedure, starting with a dimer of isophorone,[5] is relatively simple and can be carried out on a substantial scale but yields multisubstituted products and is not applicable to the preparation of benzo- or dibenzo-fused derivatives of bicyclo[3.3.1]nonenes.

We have investigated the preparation of benzo- and dibenzo-substituted derivatives of 1-halobicyclo[3.3.1]nonenes by Friedel–Crafts cyclizations of 3-benzylcyclohexanones. The reactions of ketones **1–4** with titanium tetrachloride yielded the desired bicyclic chlorides **5**, **6a**, **7**, and **8a**, respectively, in yields ranging from 36 to 42%. In contrast, reactions of the ketones with a variety of other Lewis acids (including phosphorus pentoxide, phosphorus pentachloride, boron trifluoride, and aluminum chloride) resulted in little, if any, formation of the bicyclic ring systems.

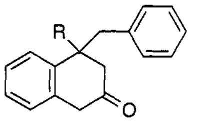
Although formation of the bridgehead chlorides by reactions of 3-benzylcyclohexanones with titanium chloride has the virtue of simplicity, better yields of halides



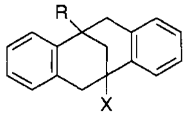
1, R = H
2, R = CH_3



5, R = H, X = Cl
6a, R = CH_3, X = Cl
b, R = CH_3, X = C_6H_5S
c, R = CH_3, X = Br



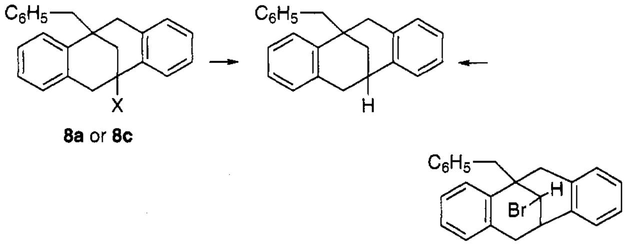
3, R = CH_3
4, R = $CH_2C_6H_5$



7, R = CH_3, X = Cl
8a, R = $CH_2C_6H_5$, X = Cl
b, R = $CH_2C_6H_5$, X = C_6H_5S
c, R = $CH_2C_6H_5$, X = Br

6a and **8a** were obtained by a two-step process in which the ketones were first cyclized to form bridgehead sulfides. We found that while no reaction occurred when 3-benzylcyclohexanones were treated with phosphorus pentoxide alone, the phosphorus pentoxide-catalyzed reactions of ketones **2** and **4** with the thiophenol resulted in efficient cyclizations, forming the 1-(phenylthio)bicyclononane derivatives **6b** and **8b** in yields of 71 and 78%, respectively. Reactions of **6b** and **8b** with 2 equiv of sulfuryl chloride converted them to the bridgehead chlorides in yields of over 80%. Similarly, reactions of **6b** and **8b** with bromine formed bromides **6c** and **8c**, in high yields.

The products of these reactions were characterized by their ^1H NMR and IR spectra and by their elemental analyses. In addition, the nature of the ring skeletons of **8a** and **8c** was demonstrated by their reduction by sodium in 2-methyl-2-propanol (or, in the case of **8c**, by lithium aluminum hydride) to yield the parent hydrocarbon. This hydrocarbon was identical with the product from reduction of bromide **9**, the structure of which had previously been established by X-ray crystallography,[6] by sodium in 2-methyl-2-propanol.



8a or **8c**

9

The reactions of Lewis acids with 3-allylcyclohexanone were also studied, in the hope of preparing 1-halobicyclo[3.3.1]nonenes lacking fused aromatic rings. However, no pure product could be obtained from the reaction of 3-allylcyclohexanone with titanium tetrachloride. Reaction with excess thiophenol and phosphorus pentoxide yielded a bis(phenylthio) product (49% yield), assigned structure **10** on the basis of its method of synthesis, spectra, and conversion to the known unsaturated chlorides **13a** and **13b** (see below). The **exo** geometry was

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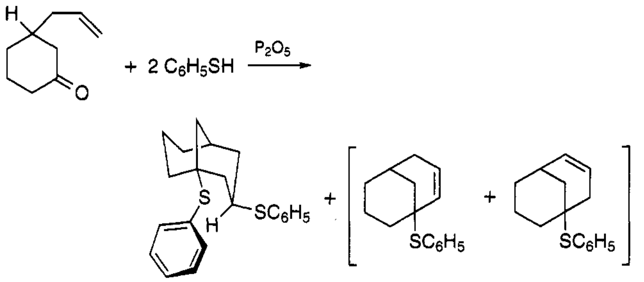
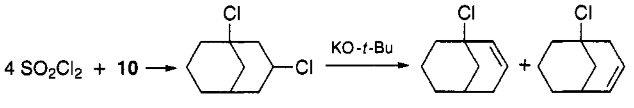


10 **11a** **11b**

assigned on the basis of the known[8] propensity of 3-bicyclo[3.3.1]nonanyl cations to yield the more stable exo derivatives on reactions with nucleophiles. (An interesting feature of the ^{1}H NMR spectrum of **10** was the presence of a signal for a single **ortho** hydrogen downfield from the signals for the other aromatic hydrogens, indicating restricted rotation around a sulfur–phenyl bond.)

In addition to **10**, unsaturated products, apparently containing one phenylthio group per molecule, were formed in ca. 25% yield. The positions of the vinyl protons[3] suggested that these products consisted of a ca. 1:1 mixture of **11a** and **11b**.

Reaction of **10** with 4 mol of sulfuryl chloride yielded a product with an ^{1}H NMR signal appropriate for the C3 hydrogen of the desired dichloride **12** (see Experimental Section). However, this compound could not be completely separated from aromatic byproducts. Stirring the crude chlorination product with potassium *tert*-butoxide in 2-methyl-2-propanol, followed by chromatography on silica gel, yielded a 2:1 mixture of the unsaturated chlorides **13a** and **13b**.[3]



12 **13a** **13b**

Experimental Section

Mp's and bp's are corrected. ^{1}H NMR spectra were taken in deuteriochloroform solutions employing TMS as an internal reference, on a 200 MHz instrument. IR spectra were taken on a FTIR spectrometer. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory.

3-Benzyl-2-cyclohexen-1-one. A solution of benzylmagnesium chloride, prepared from 4.68 g (0.20 mol) of triply sublimed Mg and 25.3 g (0.20 mol) of freshly distilled benzyl chloride in 100 mL of anhydrous ether, was stirred under nitrogen and cooled by an ice bath while a solution of 3-ethoxy-2-cyclohexen-1-one (24.0 g, 0.171 mol) in 80 mL of anhydrous ether was added over the course of 0.5 h. After completion of the addition the mixture was stirred at 0 °C for an additional 0.5 h. Saturated ammonium chloride solution was added carefully, the layers were separated, the aqueous layer was extracted with ether, and the combined ether solutions were washed with aqueous sodium chloride solution. The ether layer was dried over anhydrous magnesium sulfate and filtered and the solvent evaporated to give 31.0 g of a brown oil. A portion (10.0 g) of the crude product was chromatographed on silica gel, eluting with ether–petroleum ether (1:1), to yield **3-benzyl-2-cyclohexen-1-one** (9.1 g, 0.049 mol, 87% based on amount chromatographed) as a pale yellow oil. ^{1}H NMR: δ 1.98 (m, 2H), 2.89 (m, 4H), 3.51 (s, 2H), 5.87 (t, J = 1.4 Hz, 1H), 7.17 (m, 3H), 7.29 (m, 2H). IR (neat): 701, 747.5, 1127, 1251, 1454, 1624, 1670 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.94; H, 7.56.

3-Benzyl-3-methylcyclohexanone. Cuprous iodide (10.2 g, 0.054 mol) was added to 240 mL of anhydrous ether and the mixture stirred rapidly (magnetic stirrer) under nitrogen and cooled in a dry ice–acetone bath. A solution of methyllithium in ether (1.4 M, 80 mL, 0.108 mol) was added. The temperature was allowed to rise to 0 °C, and a solution of 3-benzyl-2-cyclohexen-1-one (6.70 g, 0.036 mol) in 240 mL of anhydrous ether was added over the course of 1 h. Stirring was continued at 0 °C for an additional 40 min, and the reaction mixture was then added to 500 mL of cold, saturated ammonium chloride solution. The layers were separated, the organic layer was extracted with 100 mL of ether, and the combined organic layers washed three times with brine. The organic layer was dried over anhydrous magnesium sulfate and filtered and the solvent evaporated. The crude product was chromatographed on silica gel, eluting with ether–petroleum ether (1:3) to yield **3-benzyl-3-methylcyclohexanone** (4.98 g, 0.025 nmol, 68%). ^{1}H NMR: δ 0.83 (s, 3H), 1.4–1.6 (m, 2H), 1.65–2.05 (m, 3H), 2.15–2.25 (m, 3H), 2.50 (d, J = 12.5 Hz, 1H), 2.52 (d, J = 12.5 Hz, 1H), 7.05 (m, 2H), 7.20 (m, 3H). IR (neat): 703, 733, 757, 911, 1453, 1709 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O$: C, 83.17; H, 8.92. Found: C, 83.09; H, 9.01.

Reaction of 3-Benzylcyclohexanones with Titanium Tetrachloride (General Procedure). A solution containing 2–4 mmol of 3-benzylcyclohexanone[9] or of a 3-benzylcyclohexanone derivative (ketones **2**–**4**) in ca. 7 mL of methylene chloride (ACS reagent grade) in a round bottom flask fitted with a drying tube containing anhydrous calcium sulfate was stirred by a magnetic stirrer and cooled to 0 °C. A solution of 4–8 mmol of titanium tetrachloride in 2 mL of methylene chloride was added in one portion, and stirring of the cold solution was continued for 3 h. The reaction mixture was poured into a mixture of ice and water and extracted with ether. The organic layer was washed with water and dried over magnesium sulfate and the solvent evaporated. The resulting mixture was chromatographed on silica gel, eluting with petroleum ether to yield a 1-chlorobicyclo[3.3.1]nonane derivative.

Chloride **5** was obtained as a colorless oil (36% yield). ^{1}H NMR: δ 1.0–1.3 (m, 1H), 1.5–1.75 (m, 3H), 2.1–2.2 (m, 3H), 2.25–2.35 (m, 1H), 2.4–2.4 (m, 1H), 2.62 (d, J = 17.9 Hz, 1H), 3.21 (dd, J = 17.9, 6.7 Hz, 1H), 7.0–7.1 (m, 1H), 7.15–7.25 (m, 2H), 7.55–7.62 (m, 1H). IR (neat): 565, 658, 721, 755, 769, 780, 833, 878, 903, 915, 941, 1012, 1032, 1219, 1297, 1319, 1427, 1450, 1485 cm^{-1}. Anal. Calcd for $C_{13}H_{15}Cl$: C, 75.55; H, 7.26. Found: C, 77.33; H, 7.50.

Chloride **6a** was obtained as a colorless oil (39% yield). ^{1}H NMR: δ 1.08 (s, 3H), 1.22–1.35 (m, 1H), 1.42–1.59 (m, 2H), 1.96–2.04 (m, 4H), 2.27 (d, J = 12.1 Hz, 1H), 2.62 (d, J = 17.7 Hz, 1H), 2.80 (d, J = 17.7 Hz, 1H), 6.97–7.03 (m, 1H), 7.12–7.20 (m, 2H), 7.66–7.71 (m, 1H). IR (neat): 1489, 1462, 1431, 1384, 1321, 1304, 1000, 927, 919, 859, 833, 774, 759, 719, 660, 567 cm^{-1}. Anal. Calcd for $C_{14}H_{17}Cl$: C, 76.19; H, 7.87. Found: C, 76.55; H, 7.98.

Chloride **7** was obtained as a white solid. Mp: 112–113 °C (from ethanol) in 42% yield. ^{1}H NMR: δ 1.55 (s, 3H), 2.48 (d, J = 18 Hz, 1H), 2.53 (d, J = 18 Hz, 1H), 2.81 (d, J = 16.3 Hz, 1H), 3.08 (d, J = 16.3 Hz, 1H), 3.41 (d, J = 15.5 Hz, 1H), 3.67 (d, J = 15.5 Hz, 1H), 6.8–6.9 (m, 2H), 6.95–7.25 (m, 4H), 7.37 (dd, J = 7.8, 1.3 Hz, 1H), 7.80 (dd, J = 7.9 Hz, 1.3, 1H). IR (mineral oil): 572, 579, 714, 740, 782, 874, 1294, 1321, 1375, 1451, 1489 cm^{-1}. Anal. Calcd for $C_{18}H_{17}Cl$: C, 80.45; H, 6.33; Cl, 13.22. Found: C, 80.69; H, 6.51; Cl, 13.03.

Chloride **8a** was obtained in 40% yield as white crystals. Mp: 163–165 °C (from ethanol). ^{1}H NMR: δ 2.29 (dd, J = 12.2, 2.7 Hz, 1H), 2.48 (dd, J = 12.2, 2.7 Hz, 1H), 2.84 (dd, J = 16.0, 2.4 Hz, 1H), 3.19–3.64 (m including a d, J = 2.6 Hz, 4H), 3.59 (d, J = 15.4 Hz, 1H), 6.85 (apparent d, J = 7.2 Hz, 2H), 7.0–7.3 (m, 9H), 7.58 (d, J = 7.9, 1H), 7.72 (dd, J = 7.8, 1.2 Hz, 1H). IR (mineral oil): 550, 577, 701, 718, 738, 757, 1146, 1176, 1186, 1379, 1450, 1489 cm^{-1}. Anal. Calcd for $C_{24}H_{21}Cl$: C, 83.60; H, 6.10. Found: C, 83.51; H, 6.03.

Reaction of Thiophenol with 1,1-Dibenzyl-2-Tetralone. A solution of 4,4-dibenzyl-2-tetralone (1.31 g, 4.00 mmol) and thiophenol (0.88 g, 8.0 mmol) in 20 mL of methylene chloride (ACS reagent grade) was cooled to 15 °C in a round bottom flask

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fitted with an air cooled reflux condensor and a drying tube containing anhydrous calcium chloride and stirred by a magnetic stirrer. Phosphorus pentoxide (2.20 g, 12.0 mmol) was added and stirring continued for 0.5 h. The mixture was diluted with 100 mL of ether, and magnesium sulfate (ca. 3 g) was added to facilitate filtration. The mixture was filtered under vaccuum and the solid residue washed with ether. The combined ether solutions were extracted three times with 50 mL portions of 10% sodium hydroxide solution and then washed with water and dried over magnesium sulfate. The mixture was filtered, the solvent evaporated, and the resulting brown solid recrystallized from 1:1 ethanol–chloroform to yield the bicyclic product **8b** (1.32 g, 3.15 mmol, 79%) as white crystals. Mp: 184.5–185 °C. ^{1}H NMR: δ 1.92 (s, 2H), 2.75 (d, J = 15.9 Hz, 1H), 3.01–3.15 (m, 4H), 3.27 (d, J = 15.6, 1H), 6.98–7.38 (m, 16H), 7.50 (d, J = 7.8, 1H), 7.92 (d, J = 7.7, 1H). IR (KBr pellet): 640, 698 (s), 737 (s), 753 (vs), 839, 924, 956, 981, 1027, 1066, 1097, 1305 cm^{-1}. Anal. Calcd for $C_{30}H_{26}S$: C, 86.12; H, 6.22; S, 7.66. Found: C, 85.86; H, 6.27; S, 7.42.

Compound **6b**. Mp: 79–80 °C (from 1:1 chloroform–ethanol) was prepared in a similar manner in 81% yield, starting with 3-benzyl-3-methylcyclohexanone. ^{1}H NMR: δ 0.95 (s, 3H), 1.0–1.3 (m, 2H), 1.36–1.76 (m, 5H), 1.94 (d, J = 12.4 Hz, 1H), 2.56 (d, J = 17.7 Hz, 1H), 2.71 (d, J = 17.7 Hz, 1H), 7.0–7.35 (m, 8H), 7.99 (d, J = 8.1 Hz, 1H). IR (KBr pellet): 508, 687 (s), 705 (s), 723, 745 (s), 765 (s), 930, 970, 1025, 1040, 1067, 1128, 1158, 1172, 1210, 1251, 1304, 1323, 1380, 1417, 1436 (s), 1447, 1473, 1481, 1570 cm^{-1}. Anal. Calcd for $C_{20}H_{22}S$: C, 81.63; H, 7.48. Found: C, 82.47; H, 7.66.

Reaction of 8b with Sulfuryl Chloride. A solution of sulfuryl chloride (0.54 g, 4.0 mmol) in 4 mL of methylene chloride (ACS reagent grade) was cooled to 0 °C and slowly added to an ice-cold, stirred solution of **8b** (0.85 g, 2.03 mmol) in 20 mL of methylene chloride. The temperature was kept at 0 °C while stirring was continued for 3 h. The reaction mixture was diluted with 100 mL of ether and washed with aqueous sodium bicarbonate solution and then with water and the organic layer dried over magnesium sulfate and filtered. The solvent was evaporated to yield 0.88 g of a pale yellow solid, which was recrystallized from chloroform/ethanol to yield (**8a** (0.60 g, 86%) as a colorless solid. Chloride **6a** was prepared (80% yield) in a similar manner from **6b**, except that stirring was maintained for only 1 h before workup.

Reaction of Bromine with 8b. A solution of **8b** (0.20 g, 0.48 mmol) in 5 mL of benzene was stirred (magnetic stirrer) in a round bottom flask with an air-cooled reflux condenser. A solution of bromine (0.17 g, 1.05 mmol) in 2.7 mL of reagent grade carbon tetrachloride was added rapidly, and the solution was stirred at room temperature for 4 h. It was then diluted with 50 mL of ether, washed with sodium bisulfite solution and then with water, dried over magnesium sulfate, and filtered. Evaporation of the solvent left 0.35 g of a viscous oil. Chromatography on silica gel, eluting with petroleum ether containing from 5 to 12% of methylene chloride, followed by recrystallization from absolute ethanol yielded bromide **8c** (0.15 g, 0.39 mmol, 81%) as white needles. Mp: 157–158 °C. ^{1}H NMR: δ 2.51 (dd, J = 12.2, 2.7 Hz, 1H), 2.59 (dd, J = 12.2, 2.5 Hz, 1H), 2.80 (dd, J = 16.0, 2.4 Hz, 1H), 3.17–3.27 (m, 3H), 3.48 (dd, J = 15.4, 2.6 Hz, 1H), 3.80 (d, J = 15.4 Hz, 1H), 6.82 (apparent t, J = 6.6 Hz, 1H), 7.00–7.26 (m, 9H), 7.55 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H). IR (KBr pellet): 525, 580, 642, 700 (s), 724 (s), 738 (s), 752 (vs), 768 (s), 914, 1030, 1452 (s), 1487 (s), 1494, 1601 cm^{-1}. Anal. Calcd for $C_{24}H_{21}Br$: C, 74.04; H, 5.40. Found: C, 73.91; H, 5.60.

A similar procedure, except that chromatography was carried out with petroleum ether as eluent, yielded bromide **6c** (69% yield) as a colorless oil. ^{1}H NMR: δ 1.05 (s, 3H), 1.24–1.60 (m, 4H), 2.18–2.29 (m, 3H), 2.49 (d, J = 18 Hz), 1H), 2.58 (d, J = 17.7 Hz, 1H), 2.83 (d, J = 17.7 Hz, 1H), 6.95–7.00 (m, 1H), 7.10–7.20 (m, 2H), 7.72–7.77 (m, 1H). IR (neat): 618, 6.96, 722 (s), 740 (s), 763 (s), 833, 879, 916, 1214, 1321, 1450, 1484 cm^{-1}. Anal. Calcd for $C_{14}H_{17}Br$: C, 63.40; H, 6.41. Found: C, 63.16; H, 6.45.

Reduction of 8c by Sodium in 2-methyl-2-propanol. Bromide **8c** (0.80 g, 2.07 mmol) and 2-methyl-2-propanol (0.78 g, 10.6 mmol) were dissolved in 20 mL of anhydrous tetrahydrofuran in a round bottom flask fitted with a reflux condenser and a drying tube containing anhydrous calcium sulfate, and sodium metal (0.25 g, 10.9 mmol) was added. The mixture was heated at reflux until the sodium had been completely consumed. The reaction mixture was cooled to room temperature, diluted with 100 mL of ether, washed with water, and dried over magnesium sulfate. After evaporation of the solvent the resulting solid was recrystallized from absolute ethanol to yield a hydrocarbon (0.55 g, 1.77 mmol, 86%). Mp: 135–136 °C. ^{1}H NMR: δ 1.71 (dd, J = 12.5, 4.2 Hz, 1H), 1.97 (d, J = 12.5 Hz, 1H), 2.76 (d, J = 16.8 Hz, 1H), 2.82 (d, J = 14.8 Hz, 1H), 3.03 (d, J = 16.8 Hz, 1H), 3.2–3.27 (m, 5H), 6.7–7.2 (m, 11 H), 7.59 (d, J = 7.6 Hz, 1H). IR (KBr pellet): 510, 553, 569, 641, 699 (s), 732 (s), 753 (vs), 767 (s), 782, 953, 971, 1030, 1037, 1054, 1077, 1251, 1301, 1319, 1427, 1450 (s), 1490 (s), 1576 cm^{-1}. Anal. Calcd for $C_{24}H_{22}$: C, 92.90; H, 7.10. Found: C, 92.79; H, 7.22.

Reduction of chloride **8a** and bromide **10** under similar conditions yielded the same hydrocarbon in yields of 76 and 79%, respectively.

Reaction of 3-Allylcyclohexanone with Thiophenol. A solution of 3-allylcyclohexanone[9] (1.00 g, 7.25 mmol) and thiophenol (2.39 g, 21.8 mmol) in 30 mL of reagent grade methylene chloride was maintained at 15–20 °C in a round bottom flask fitted with a reflux condenser stopped with a drying tube containing anhydrous magnesium sulfate. Phosphorus pentoxide (3.0 g, 16.3 mmol) was added over the course of 5 min. Stirring was continued for 48 h, until TLC analysis showed the starting ketone to have disappeared. The reaction mixture was diluted with 50 mL of ether, washed three times with sodium hydroxide solution and then with water, and dried over magnesium sulfate and the solvent evaporated. The resulting viscous brown oil was chromatographed on silica gel, eluting with petroleum ether to yield an apparent mixture of **1-(phenylthio)bicyclo[3.3.1]non-2-ene** (^{1}H NMR: δ 5.67–5.90, m, C2 and C3) and **1-(phenylthio)bicyclo[3.3.1]non-3-ene** (^{1}H NMR: δ 5.57–5.65, m, C3 and C4) totalling 0.42 g (1.83 mmol, 25%), as a colorless oil. Anal. Calcd for $C_{15}H_{18}S$: C, 78.26; H, 7.83. Found: C, 78.03; H, 8.05.

Further elution yielded **1,3-bis(phenylthio)bicyclo[3.3.1]-nonane (11)** (1.20 g, 3.53 mmol, 49%) as white needles. Mp: 89–90 °C. ^{1}H NMR: δ 1.32 (m, 13H), 3.78 (tt, J = 12.0, 6.0 Hz, 1H), 7.2–7.5 (m, 9H), 7.71 (dd, J = 7.9, 1.4 Hz, 1H). IR (KBr pellet): 693 (s), 704, 749 (s), 1025, 1045, 1067, 1089, 1306, 1353, 1438 (s), 1459, 1583 cm^{-1}. Anal. Calcd for $C_{21}H_{24}S_2$: C, 74.12; H, 7.06. Found: C, 74.04; H, 7.23.

Chlorination and Dehydrochlorination of 11. A cold solution of sulfuryl chloride (0.95 g, 7.03 mmol) in 5 mL of methylene chloride was added slowly to a stirred solution of **11** (0.59 g, 1.73 mmol) in 2 mL of methylene chloride. Stirring was continued at 0 °C for 2 h. After workup as described for the chlorination of **8b**, the resulting brown oil (0.48 g) was chromatographed on silica gel, eluting with petroleum ether, to yield a colorless oil (0.31 g), which had a ^{1}H NMR signal at δ 4.62 (tt, J = 12.0, 6.0 Hz). The oil was dissolved in 2-methyl-2-propanol (2 mL), and potassium *tert*-butoxide (0.20 g, 1.79 mmol) was added. The mixture was shaken and allowed to stand at room temperature for 4 h. Ether (15 mL) was added, and the mixture was washed twice with water, dried over magnesium sulfate, and filtered and the solvent evaporated. The residue was chromatographed on silica, eluting with petroleum ether, to yield 0.12 g of a 2:1 mixture of chlorides **13a** and **13b**.

JO9505987