tified with the above 1:1 complex by IR and ^{1}H NMR spectra. Reaction of **5** (141 mg, 0.50 mmol) and **24** (448 mg, 2.5 mmol) in chloroform (10 mL) at room temperature for 3 days also gave the same complex (225 mg, 97%).

Kinetics. The kinetic run was initiated by mixing 1-2 mL of diene (**17a-d**) stock solution and 1-2 mL of dienophile (**5**) solution into a 10 × 10 mm quartz cell, which was thermostated with flowing water at a given temperature. In the case of the reaction of **5** and **17a-c**, the diene concentration was in large excess over that of dienophile and the rates were measured by following the disappearance of the CT bands at 500-550 nm. The pseudo-first-order rate constants were calculated from a plot of ln $[(A_t - A_\infty)/(A_0 - A_\infty)]$ vs. time by a least-squares method, where A_t is the absorbance at time t and A_∞ is the absorbance after 10 half-lives. The second-order rate constants (k_2) were obtained in the usual manner. The treatment of Andrews and Keefer[41] was followed in the calculation of the equilibrium constants.

The rates of the reaction of **5** with **17d** which showed no CT bands were measured by following the disappearance of the dienophile **5** at 600-630 nm. The initial concentrations of **5** and **17d** used were 0.0143 M and 0.15 M, respectively, because of the low solubility of **5**. The second-order rate constants (k_2) were calculated from a plot of $(\ln [(A_0 - A_\infty)(b - a)/(A_t - A_\infty) + a] - \ln b)/(b - a)$ vs. time by a least-squares method, where A_0 and A_∞ are the same as above and a and b are the initial concentrations of **5** and **17d**, respectively. The kinetic data are listed in Tables IV-VII.[37]

Acknowledgment. We thank Dr. S. Inagaki, Gifu University, for many helpful suggestions concerning the theoretical interpretation by cyclic conjugation theory. We also thank J. Mashima and H. Yamasaki for technical assistance and Kureha Chemical Ind. Co., for partial financial support to E.O. Calculations have been performed at the Computing Centers of Hokkaido University and the Institute for Molecular Sciences.

Registry No. 2, 63401-20-7; **4**, 290-79-9; **5**, 16114-35-5; **5·24** (complex 1:1), 83572-95-6; **6**, 16114-41-3; **8**, 2448-55-7; **15**, 26638-36-5; **16**, 108-31-6; **17a**, 120-12-7; **17b**, 779-02-2; **17c**, 781-43-1; **17d**, 642-31-9; **17e**, 602-60-8; **18a**, 16265-74-0; **18b**, 83561-79-9; **18c**, 83561-80-2; **18d**, 83561-81-3; **19**, 83561-82-4; **20**, 83561-83-5; **21**, 83561-84-6; **22**, 83561-85-7; **23a**, 83561-86-8; **23c**, 83572-94-5; **24**, 260-94-6; **25**, 92-82-0; *N*-methylsuccinamic acid, 56269-39-7; *N*-*n*-propylsuccinamic acid, 61283-60-1; *N*-*tert*-butylsuccinamic acid, 6622-06-6.

Supplementary Material Available: LUMO coefficients of 1,4-dithiin and derivatives (**4-6, 8, 15**) and maleic anhydride (**16**) calculated by MNDO (Table II), and the second-order rate constants for cycloaddition of bisimide **5** with 9-methyl- and 9-formylanthracene (**17b, 17d**) in various solvents (Table VII) (2 pages). Ordering information is given on any current masthead page.

Single and Double Ring-Closure Reactions of Dianions of Bis(diphenyl thioacetals). A New, Synthetically Useful Principle of Carbene Generation and Intramolecular Capture

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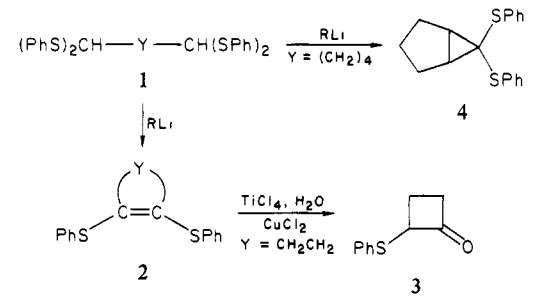
Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. *Received April 5, 1982*

Abstract: A mechanistic study described herein leads to the new, potentially useful general principle that normally stable anions of diphenyl thioacetals decompose to carbenes when they are generated in a molecule with a second anionic site nearby; it also appears that the second anionic site may be influential in determining the selectivity of the carbene. Strong evidence is presented that dianions are intermediates in the alkyllithium-induced conversions of 1,1,4,4-tetrakis(phenylthio)butane (**1A**) and 1,1,6,6-tetrakis(phenylthio)hexane (**1C**) to 1,2-bis(phenylthio)cyclobutene (**2A**) and 6,6-bis(phenylthio)bicyclo[3.1.0]hexane (**4**), respectively. The use of *p*-*tert*-butyl groups as aryl labels leads to the conclusion that the carbenic carbon atom of the assumed anion carbene intermediate **6**, formed by ejection of thiophenoxide ion from the dianion (**5**) of **1A**, bonds with sulfur to produce a 5-membered ring anion ylide (**8**), which rearranges to **2A**. Similar labeling experiments are interpreted as indicating that the carbenic carbon atom of the corresponding anion carbene (**14**), derived from **1C**, inserts into the weak CH bond adjacent to the negatively charged carbon atom to produce a cyclopentyl thioacetal anion (**15**), which ejects a thiophenoxide ion to yield the bicyclic product **4**. The new principle has been dramatically demonstrated by treating 5,5-bis(phenylthio)-1-pentanol (**21**) with *sec*-butyllithium whereby the geometric isomers of 2-(phenylthio)cyclopentanol (**24**) are produced, presumably via insertion of the carbenic carbon atom of the anion carbene **23** into the reactive CH bond of the carbinol anion.

A remarkable ring closure reaction (**1A** → **2A** and **1B** → **2B**)



A, Y = CH_2CH_2; B, Y = $CH_2CH(CH_3)CH_2$; C, Y = $(CH_2)_4$

has been reported recently from this laboratory.[1] This type of ring closure is of interest not only because of its novelty but because **3**, the hydrolysis product of **2A**,[2] is synthetically useful as a surrogate for cyclobutanone[2] and as a precursor of 2-methoxy-3-(phenylthio)-1,3-butadiene.[3] We now report a still more remarkable ring closure of a bis(dithioacetal), we present a mechanistic study of these highly unusual ring closures, and, most importantly, we enunciate a new principle of carbene generation and use, which should have wide applicability in synthetic organic chemistry; the principle is dramatically illustrated by the cyclization of a straight-chain primary alcohol terminated by a thioacetal group, such cyclization involving unprecedented CC bond formation between carbinol and thioacetal carbon atoms.

Results and Discussion

When **1C**, prepared by the reaction of 1,4-diiodobutane with bis(phenylthio)methyllithium, was treated with 2-4 equiv of methyllithium in THF containing 2-4 equiv of tetramethyl-

(1) Cohen, T.; Ouellette, D.; Daniewski, W. M. *Tetrahedron Lett.* **1978**, 5063.

(2) Cohen, T.; Ouellette, D.; Senaratne, K. P. A.; Yu, L.-C. *Tetrahedron Lett.* **1981**, *22*, 3377.

(3) Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3548.

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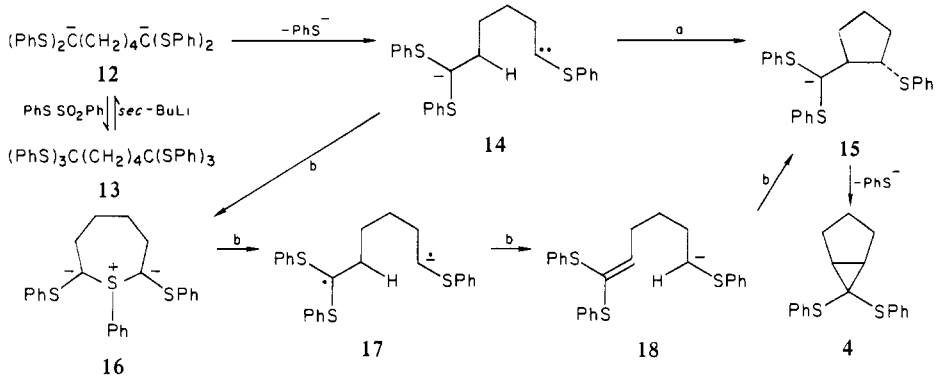
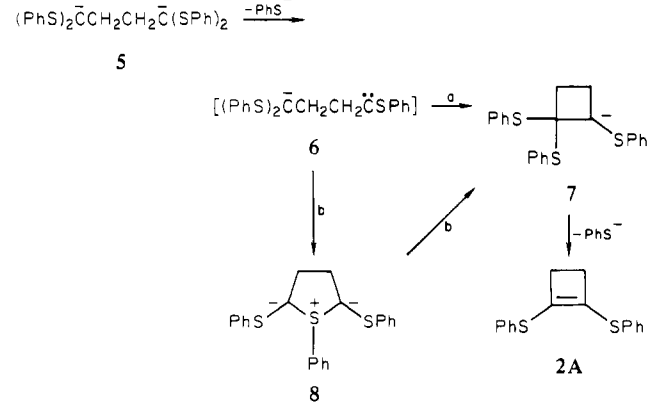
Scheme I



ethylenediamine (TMEDA) at 0 °C for 4–6 h, **2C** was isolated as a pale yellow oil in less than 10% yield. The major product, isolated in yields up to 40% by medium-pressure liquid chromatography, is an isomer of **2C**, 6,6-bis(phenylthio)bicyclo[3.1.0]-hexane (**4**), the product of a *double ring closure*; the spectroscopic properties of **4** were found to be identical with those of an authentic sample prepared by a modification of the procedure of Braun and Seebach.[4]

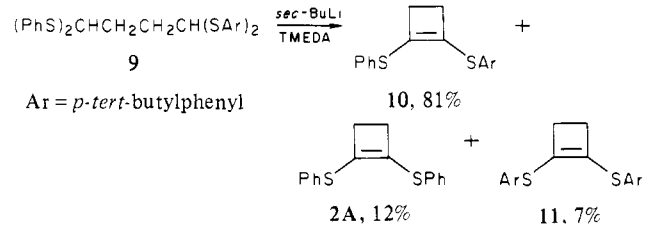
In view of the unprecedented nature of these ring closures, mechanistic information, which might reveal a new synthetically useful principle, was sought. We had already ruled out a step involving an intramolecular S_N2 displacement of PhS^- in the monoanion of **1B**.[1] An attempt to prepare the suspected intermediate, dianion (**5**) of **1A**, by treatment of the latter with 2 equiv of *sec*-butyllithium, was only partially successful because the rate of production of **5** is only slightly faster than the rate of decomposition of **5** to cyclobutene **2A**; as a result, a portion of the alkyllithium is destroyed by reaction with **2A** [2] and is thus unavailable to execute the removal of the second proton from **1A**. When the reaction mixture was quenched with D_2O after 1 h at −45 °C, the ratio of **1A** to **2A** produced was about 91:9 (the conjugate base of the latter is known to suffer some decomposition[2]) and the labeling of recovered starting material indicates that a ratio of approximately 2:1 of dianion (**5**) to monoanion had been present. If, instead of being quenched, the reaction mixture was warmed to 0 °C and quenched with D_2O after 1 h, 55% of **2A** was isolated along with 20% of recovered bis(dithioacetal) consisting of 14% undeuterated, 79% monodeuterated, and only 7% dideuterated material. The most likely explanation of this result is that only the dianion is converted to **2A**. The inertness of the monoanion is not surprising in view of our finding that the lithio derivative of 1,1-bis(phenylthio)propane is not completely decomposed even after *17 h* at 0 °C.

Since it is difficult to imagine a bond being established between two negatively charged termini of the dianion chain of **5**, it is



assumed that a key step is ejection of a thiophenoxide ion to produce the sulfur-stabilized carbene **6**; literature precedents for carbene production from special α-lithio phenylthio ethers have been cited.[1] Two conceivable paths for **6** involve quenching of the carbene by (a) the negatively charged carbon atom[5] to produce **7** or by (b) the sulfur atom to produce the ylide anion **8**.[6–8] The latter could undergo a Stevens rearrangement[9] to **7**, which, by ejection of a thiophenoxide ion, would yield **2A**.

These two pathways are distinguishable by labeling the two aromatic rings of one of the thioacetal functions of **1A**. Path a implies that the **2A** analogue produced would be homogeneous, possessing one phenyl and one labeled aryl group. If it assumed that the label does not influence the chemical behavior, path b implies that at least $^1/_8$ of the product should contain two phenyl rings and another $^1/_8$ should contain two labeled rings; if the conversion of **6** to **8** is reversible, a greater degree of aryl group shuffling should occur. When bis(thioacetal) **9**, in which the two aryl rings of one of the thioacetal functions are labeled with *p-tert*-butyl groups,[10] was treated under the reaction conditions, the cyclobutene product was shown by mass spectrometry to consist of all three possible analogues (**10**, **2A**, and **11**). These could



be separated and quantitatively determined by reversed-phase HPLC using UV detection. The results are shown in the equation.[11] Considering errors in analysis[12] and the possibility that the *tert*-butyl groups may have some influence on the rates of bond formation and cleavage, the results are in satisfactory agreement with path b. The possibility that the aryl group shuffling occurred not via analogues of **8** but by reversibility of the carbene production (analogous to **5** ⇌ **6** + PhS^-) was precluded by treating **1A** with

(4) Braun, M.; Seebach, D. *Chem. Ber.* **1976**, *109*, 669. We thank Dr. James Matz for performing this experiment: Matz, J. R. Ph.D. Thesis, University of Pittsburgh, 1981; p 91.

(5) For evidence of intermolecular carbanion attack on sulfur-stabilized carbenes, see: Beak, P.; Worley, J. W. *J. Am. Chem. Soc.* **1972**, *94*, 597. Leger, L.; Saquet, M. *Bull. Soc. Chem. Fr.* **1975**, 657.

(6) Carbenes are frequently trapped by divalent sulfur and intramolecular examples are known: Ando, W. *Acc. Chem. Res.* **1977**, *10*, 179.

(7) Anion ylides are known species: Wallenfels, K.; Friedrich, K.; Rieser, J. *Liebigs Ann. Chem.* **1976**, 656. Rieser, J.; Friedrich, K. *Ibid.* **1976**, 641. Rieser, J.; Friedrich, K. *Ibid.* **1976**, 648. Roush, D. M.; Price, E. M.; Templeton, L. K.; Heathcock, C. H. *J. Am. Chem. Soc.* **1979**, *101*, 2971.

(8) Five-member ring ylide formation by intramolecular attack of an alkyl halide on the sulfur atom of a sulfur-stabilized carbanion followed by rearrangement to a four-member ring has been invoked. Ogura, K.; Yamashita, M.; Furkawa, S.; Suzuki, M.; Tsuchihashi, G. *Tetrahedron Lett.* **1975**, 2767.

(9) Lepley, A. R.; Giumanini, A. G. In "Mechanisms of Molecular Migrations"; Thyagarajan, B. S., Ed.; Interscience: New York, 1971; Vol. 3, p 297.

(10) *p*-Methyl groups were found not to be useful due to deprotonation.

(11) An authentic sample of **11** could be prepared from the bis(thioacetal) possessing four *tert*-butylphenyl groups.

(12) The major error came from impurities in authentic **2A** which could not be separated from **2A** and which became apparent only upon efficient HPLC.

sec-butyllithium in THF containing excess lithium *p*-(*tert*-butylthio)phenoxide, isolating unreacted bis(thioacetal) after 95% reaction, and finding that neither the bis(thioacetal) nor the ring-closed product contained *p*-*tert*-butylphenyl groups (MS and NMR evidence).

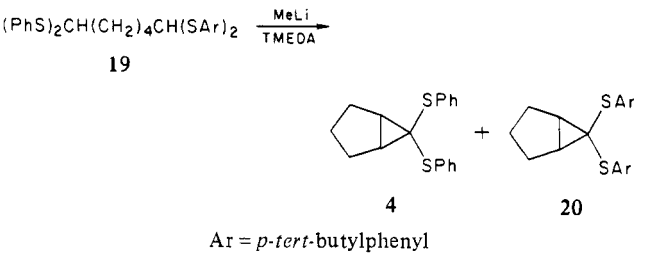
When **1C** was treated with 2.1 equiv of *sec*-butyllithium in THF containing 2.0 equiv of TMEDA at −45 °C for 1 h and the mixture quenched with D_2O, the ratio of dideuterated to monodeuterated **1C** was 85/15 and no **2C** or **4** was evident.[13] If the mixture was quenched with phenyl benzenethiosulfonate[14] instead of D_2O, a 62% yield of highly crystalline 1,1,1,3,3,3-hexakis(phenylthio)-hexane (**13**) was produced. If instead of being quenched, the mixture containing mainly dianion **12** was allowed to warm to 0 °C, a 48% yield of **4** could be isolated after 6 h. When the hexakis(phenylthio)hexane **13** was treated with 2 equiv of *sec*-butyllithium for 1 h at −50 °C, a solution containing dianion **12** and *sec*-butylphenyl sulfide was formed (workup of a portion yielded only the latter and 95% of **1C**); when this solution was warmed to 0 °C, the yield of **4** formed after 5 hours was comparable to that obtained by deprotonation of **1C**. It is thus clear that both **2a** and **4** are produced via dianion intermediates.

Once again, it is reasonably safe to assume that a carbene anion (**14**) is an intermediate in the production of **4** (Scheme I). Furthermore, it is difficult to conceive of an immediate precursor of **4** other than **15**. We have already demonstrated a very close analogue of the conversion of **15** to **4**.[15]

A most attractive route (path a) from **14** to **15** involves an insertion of the carbene into the weakened CH bond adjacent to the negatively charged carbon atom; the weakness of bonds to carbon atoms which are attached to negatively charged atoms has been studied and elegantly exploited by Evans.[16] An intermolecular analogue of such an insertion into the weakened carbinyl CH bond of an alkoxide has recently been reported[17] and intermolecular examples of carbene insertion into the β-CH bonds of organometallics are known.[18] Models indicate that steric hindrance in the transition state for insertion, whether concerted or stepwise, would dictate the production mainly of the trans ring-closed product **15**.

However, in view of the attack of sulfur on the carbene in **6**, a route through the symmetrical intermediate **16** (path b) should also be considered. As in the rearrangement of **8** to **7**, one could invoke a Stevens rearrangement, which is believed to occur via homolytic cleavage of the CS bond,[9] to convert **16** to the diradical anion **17**. In addition to the usual intramolecular radical coupling which would lead to **2C**, **17** could undergo a 1,5-hydrogen atom transfer, which should be an extremely favorable path for a 1,6-diradical. The resulting anion (**18**) could undergo an intramolecular version (**18** → **15** → **4**) of a reaction which is now well precedented in intermolecular cases.[19]

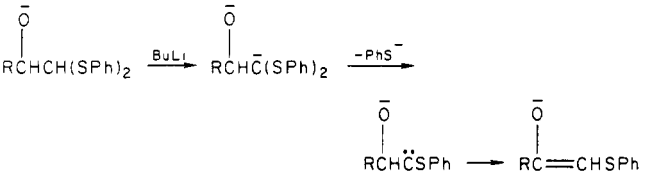
Path a implies that a bis(dithioacetal) (**19**) in which the two aryl groups of one of the thioacetal functions were labeled would produce only two bicyclic products, **4** and its analogue (**20**) in which both aryl groups were labeled. On the other hand, path b would yield only 25% each of these products and 50% of the analogue of **4** in which one phenyl group is replaced by the labeled aryl group. In the event, the labeled bis(dithioacetal) **19**[20] reacted



Ar = *p*-*tert*-butylphenyl

with methyllithium to produce **4** and **20**,[21] in approximately equal quantities as expected for path a and none of the mixed cyclopropanonethioketal which is predicted for path b. Thus, unlike the shorter chain case (**1A**), the major product in the case of **1C** occurs without the intervention of a symmetrical intermediate. The insertion pathway appears most likely, although these results do not rule out more circuitous and less precedented routes involving steps such as **14** → **17** or **14** → **18**.

Diphenyl thioacetal anions have been used extensively as nucleophiles in recent years,[4,15,19,22,23] and the products obtained, in the absence of cuprous ions,[24] rarely can be attributed to carbenes.[1] In addition to the three examples discussed here, we are aware of one other[25] which we interpret as follows:



Once again, a dianion is almost certainly involved and it forms an anion carbene, the carbenic carbon atom of which inserts into the electron-rich, weak carbinyl CH bond to yield the enolate precursor of the ketone isolated.

It is thus reasonable to postulate that the anion of a diphenyl thioacetal will yield products attributable to a carbene when the anion is generated in a molecule which bears a nearby additional negative charge. This could occur either because the electrostatic repulsion of negative charges in the same molecule increases the rate of thiophenoxide expulsion and/or because a very small amount of carbene is normally in equilibrium with such thioacetal anions, and a negative center in the carbene molecule so activates nearby atoms and bonds toward reaction with the carbene that the latter is efficiently trapped, thereby driving the equilibrium toward carbene formation; an analogy for such an equilibrium is the demonstration that $LiC(SPh)_3$ is in an unfavorable equilibrium with LiSPh and $:C(SPh)_2$.[26] Both rationalizations are consistent with our findings that at 0 °C **5** decomposes more rapidly than does the analogue **12**, in which the two negative charges are further apart, and that both decompose far faster than the anion of 1,1-bis(phenylthio)propane. Of considerable further significance in the observation that the decomposition of the latter anion, in sharp contrast to those of the dianions discussed above, yields an extensive array of products from which no one compound can be readily isolated; *this highlights the key role of the second anionic site in controlling the reactivity of the thioacetal anion and/or the derived carbene.*

We have observed in preliminary experiments carbene production from several other diphenyl thioacetal anions which were generated in molecules containing a second anionic site. One of these results, a striking example of the unorthodox bond-forming capability achievable with this concept, is a rarely observed[27]

(13) Some *sec*-butyllithium is undoubtedly consumed by thiophenoxy–lithium exchange, a reaction which we have found to be weakly competitive with proton abstraction in the case of such thioacetals.

(14) Trost, B. M.; Massiot, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 4405.

(15) Cohen, T.; Matz, J. R. *J. Org. Chem.* **1979**, *44*, 4816.

(16) Evans, D. A.; Baillargon, D. J. *Tetrahedron Lett.* **1978**, 3319. Steigerwald, M. L.; Goddard, W. A.; Evans, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1994 and references cited therein.

(17) Harada, T.; Oku, A. *J. Am. Chem. Soc.* **1981**, *103*, 5965.

(18) Landgrebe, J. A.; Mathis, R. D. *J. Am. Chem. Soc.* **1966**, *88*, 3545. Landgrebe, J. A.; Therman, D. E. *Ibid.* **1967**, *89*, 4542; **1968**, *90*, 6256; **1969**, *91*, 1759. Seyferth, D.; Damrauer, R.; Washburne, S. S. *Ibid.* **1967**, *89*, 1538. Seyferth, D.; Washburne, S. S.; Attridge, C. J.; Yamamoto, K. *Ibid.* **1970**, *92*, 4405. Seyferth, D.; Washburne, S. S. *J. Organomet. Chem.* **1966**, *5*, 389.

(19) Cohen, T.; Weisenfeld, R. B.; Gapinski, R. E. *J. Org. Chem.* **1979**, *44*, 4744.

(20) The preparation of **19** was analogous to that of **9** except that the thioacetal alcohol was prepared by treatment of dihydropyran with dry HCl in thiophenol.

(21) An authentic sample of **20** was prepared by two different methods analogous to those used to prepare **4**.

(22) Cohen, T.; Ruffner, R. J.; Shull, D. W.; Fogel, E. R.; Falck, J. R. *Org. Synth.* **1980**, *59*, 202.

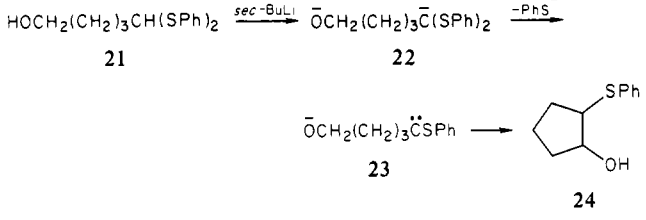
(23) Grobel, B.-T.; Seebach, D. *Synthesis* **1977**, 357.

(24) See footnote 16 of ref 1.

(25) Kuwajima, I.; Kurata, Y. *Chem. Lett.* **1972**, 291.

(26) Nitche, M.; Seebach, D.; Beck, A. K. *Chem. Ber.* **1978**, *111*, 3644. Wildschut, G. A.; Bos, H. J. T.; Brandsma, L.; Arens, J. F. *Monatsh. Chem.* **1967**, *98*, 1043.

5-membered ring formation which occurs when **21** is treated with



cis–trans isomers

sec-butyllithium at −78 °C and the dianion (**22** detectable by D_2O quenching) is warmed to 0 °C; the 5-membered rings **24**,[29] presumably formed by insertion of the carbenic carbon atoms of **23** into the activated CH bond[16,17] of the alkoxide function, are the major products. Other examples will be reported in due course.

Conclusion

While intramolecular carbene reactions have been very useful synthetically, particularly in the preparation of strained molecules, the ability to generate such carbenes has been somewhat limited, their reactions have frequently been unselective, and their synthetic utility has nearly always been restricted to the production of 3-membered rings.[28] Because of the great ease of incorporating the diphenyl thioacetal anion functionality into molecules possessing a second anionic site and the powerful role that a second anionic site is expected to exert on the selectivity of the carbene, this new concept should result in a huge class of new reactions which would be expected to find significant use in synthesis.

Experimental Section

High-pressure liquid chromatography (HPLC) was performed with a Waters Model ALC/GPC 301 with delivery system Model 6000 equipped with a Waters UK6 injector. Preparative-scale HPLC was performed at 2000 psi with columns packed with 10-μm Licosorb. Analyses were done on an Altex 5-μm octadecylsilyl reverse-phase column, 4.6 × 230 mm, or an Excalibar 5-μm silica column, 4.6 × 250 mm.

Bis(phenylthio)methane. Dry HCl gas was passed through a solution of dimethoxymethane (38.0 g, 0.499 mol) in 160 mL of thiophenol at 0 °C for 0.5 h. The mixture was then heated at reflux for 12 h and cooled, and the phases were allowed to separate. The methanol phase was discarded and the remaining liquid was diluted with ether and washed with 10% aqueous NaOH to remove the excess thiophenol. Concentration of the dried ($MgSO_4$) ether layer gave 108 g (93%) of a light yellow oil which crystallized on standing: mp 36.0–37.5 °C (reported[22] mp 35–37 °C); IR ($CHCl_3$) 1590, 1480, 1440 cm^{-1}; NMR (CCl_4, 60 MHz) δ 4.3 (s, 2 H, CH_2), 7.10–7.50 (m, 10 H, Ph); mass spectrum, (15 eV) *m/e* 232 (M^+) (99), 123 (100).

1,1,4,4-Tetrakis(phenylthio)butane (1A). Dry HCl gas was passed through a solution of 2,5-(dimethoxy)tetrahydrofuran (10 mL, 95% pure, 0.073 mol) in 150 mL of thiophenol for 7.5 h. The mixture was then stirred for an additional 12 h under argon and extracted with ether, and the excess thiophenol was removed by washing the ether layer with 10% aqueous NaOH. Concentration of the dried ($MgSO_4$) ether fractions gave, after purification by recrystallization from ethanol, 36 g (100%) of **1A** as a white solid: mp 89–91 °C; IR (KBr) 1470, 1440, 1250, 1160, 1035, 930, 830, 765, 705 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.95–2.23 (m, 4 H, CH_2), 4.10–4.40 (m, 2 H, C*H*$(SPh)_2$), 7.00–7.50 (m, 20 H, Ph); mass spectrum, (15 eV) *m/e* 490 (M^+) (2), 381 (89), 271 (100), 231 (10), 151 (10) 135 (77), 110 (11). Anal. Calcd for $C_{28}H_{26}S_4$: C, 68.52; H, 5.35. Found: C, 68.75; H, 5.48.

1,2-Bis(phenylthio)cyclobutene (2A). *sec*-Butyllithium (2.40 mL, 1.25 M in cyclohexane, 3.05 mmol) was added to a solution of **1A** (0.495 g, 1.01 mmol) and TMEDA (0.45 mL, 3.1 mmol) in 14.0 mL of anhydrous THF at −78 °C under an argon atmosphere. The solution was stirred at −78 °C for 10 min and then at 0 °C for 20 min. The reaction mixture was poured into water and extracted with ether. Rotary evaporation of the dried ($MgSO_4$) ether layer afforded 0.350 g of the crude product mixture. Purification by preparative layer chromatography afforded 0.192 g (70.4%) of **2A**: IR (film) 1580, 1475, 1440 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 2.55 (s, 4 H, CH_2), 7.10–7.50 (m, 10 H, Ph); mass spectrum, (15 eV) *m/e* 270 (M^+) (100), 237 (15), 218 (14), 161 (11); high-resolution mass spectrum calcd for $C_{16}H_{14}S_2$; *m/e* 270.0537; found, *m/e* 270.0530.

Attempted Formation of Dianion 5. To a solution of 1,1,4,4-tetrakis(phenylthio)butane (**1A**) (99.8 mg 0.204 mmol) and TMEDA (0.15 mL, 0.99 mmol) in 4.0 mL of THF at −45 °C (hexanol–dry ice) under argon was added *sec*-butyllithium (0.38 mL, 1.14 M in cyclohexane, 0.43 mmol). The resulting solution was stirred for 1 h at −45 °C and then D_2O (1.50 mL) was added. The reaction mixture was concentrated by evaporation of the THF and extracted with ether. Concentration of the dried ($MgSO_4$) extract gave 88.4 mg of crude material whose NMR integration indicated a 91:9 ratio of bis(diphenyl thioacetal) to 1,2-bis-(phenylthio)cyclobutene (**2A**) and that the recovered starting material was 65% d_2: ^1H NMR ($CDCl_3$, 60 MHz) δ 2.00–2.23 (m, 23), 2.57 (s, 2.2), 4.07–4.23 (m, 2), 7.07–7.60 (m, 133). Further analysis by HPLC (5-μm silica column, eluted with 1% ethyl acetate in hexanes, flow rate 1.0 mL/min) indicated a ratio of **1A**:**2A** of 86.14; however, there were trace impurities which eluted with **2A** and the actual ratio should be somewhat greater.

Preparation of 1,2-Bis(phenylthio)cyclobutene (2A). Quench with D_2O. *sec*-Butyllithium (1.50 mL, 1.15 M in cyclohexane, 1.73 mmol) was added to a solution of **1A** (0.399 g, 0.815 mmol) and TMEDA (0.55 mL, 3.6 mmol) in 11.0 mL of THF at −45 °C (hexanol–dry ice) under argon. The resulting solution was stirred for 1 h at −50 °C, at which time the hexanol–dry ice bath was replaced with an ice bath. After the solution had been stirred for one additional hour, the reaction was quenched with 2.0 mL of D_2O, the mixture was concentrated to remove the THF, and the concentrate was extracted with ether. Concentration of the dried ($MgSO_4$) extracts followed by flash chromatography (silica gel, eluted with 2% ethyl acetate in hexanes) gave 0.121 g (54.7%) of undeuterated **2A** whose NMR spectrum was identical with that of an authentic sample and 0.0729 g of **1A** whose NMR spectrum indicated mainly d_1; ^1H NMR ($CDCl_3$, 60 MHz) δ 1.90–2.13 (m, 16), 4.07–4.23 (m, 4), 6.90–7.50 (m, 100). Mass spectral analysis of the recovered starting material showed it to be 14.5% d_0, 78.8% d_1, and 6.7% d_2.

Preparation of 1,2-Bis((*p*-*tert*-butylphenyl)thio)cyclobutene (11). 1,1,4,4-Tetrakis((*p*-*tert*-butylphenyl)thio)butane was prepared from *p*-*tert*-butylthiophenol and 2,5-dimethoxytetrahydrofuran in the same manner as **1A**. Recrystallization of the crude product mixture from CCl_4–CH_3CN afforded a 70% yield of the bis(diaryl thioacetal) as white crystals: mp 165.5–167.0 °C; IR (KBr) 2960, 2930, 2910, 2875, 1485, 1380, 1360, 1265, 1240, 1110, 820, 790 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 1.33 (s, 36 H, CH_3), 2.00–2.20 (m, 4 H, CH_2) 4.10–4.40 (m, 2 H, C*H*$(SAr)_2$), 7.30 (s, 16 H, Ar); mass spectrum, (15 eV) *m/e* 713 (M^+) (2), 549 (91), 383 (100), 343 (19), 166 (28), 151 (34); high-resolution mass spectrum calcd for $C_{34}H_{45}S_3$ (M^+ − SAr), *m/e* 549.2683; found, *m/e* 549.2663.

1,2-Bis((*p*-*tert*-butylphenyl)thio)cyclobutene (**11**) was prepared from 1,1,4,4-tetrakis((*p*-*tert*-butylphenyl)thio)butane in an analogous manner to that described for the preparation of **2A** from **1A**. Analytically pure samples were obtained by preparative scale HPLC (10-μm Licosorb, eluted with 1% ethyl acetate in hexanes) to give a 51% yield of **11** which slowly crysallized upon storage at −25 °C: mp 39.0–42.0 °C; IR (film) 2960, 2925, 1490, 1460, 1400, 1385, 1270, 1230, 1120, 920, 825, 780 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.33 (s, 18 H, CH_3), 2.50 (s, 4 H, CH_2), 7.30 (s, 8 H, Ar); mass spectrum, (15 eV) *m/e* 382 (M^+) (100), 349 (16); high-resolution mass spectrum calcd for $C_{24}H_{30}S_2$, *m/e* 382.1789; found, *m/e* 382.1789.

3,3-Bis(phenylthio)-1-propanol. To a stirred solution of bis(phenylthio)methane (2.05 g, 8.83 mmol) in 100 mL of anhydrous THF at −23 °C was added *n*-butyllithium (6.80 mL, 1.30 M in hexane, 8.84 mmol). The resulting yellow solution was stirred for 30 min, at which time ethylene oxide (0.44 mL, 8.8 mmol), condensed from a lecture bottle, was injected with a dry ice cooled syringe. The solution was stirred for 17 h at 6 °C and was then poured into water and the mixture was extracted with ether. Rotary evaporation of the dried ($MgSO_4$) ether layer afforded 3.83 g of a crude product mixture. Purification by column chromatography (silica gel, eluted with 20% ethyl acetate in hexanes) afforded 2.2 g (90%) of 3,3-bis(phenylthio)-1-propanol: IR (film) 3650–3100 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.80–2.10 (m, 2 H, CH_2), 3.05 (br s, 1 H, OH), 3.70 (t, J = 6 Hz, 2 H, CH_2O), 4.60 (t, J = 7 Hz, 1 H, C*H*$(SPh)_2$), 7.05–7.60 (m, 10 H, Ph); mass spectrum, (15 eV) *m/e* 276 (M^+) (27), 167 (100); high-resolution mass spectrum calcd for $C_{15}H_{16}OS_2$; *m/e* 276.0643; found, *m/e* 276.0642.

3,3-Bis(phenylthio)-1-propyl Benzenesulfonate. To a solution of 3,3-bis(phenylthio)-1-propanol (0.23 g, 0.83 mmol) in 10 mL of anhydrous

(27) Reference 28a; p 321. Reference 28b; pp 236, 328.

(28) Reviews of carbenes: (a) Wulfman, D. S.; Poling, B. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1. (b) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. (c) Moss, R.; Jones, M. "Carbenes"; Wiley: New York, 1973; Vol. 1.

(29) The trans isomer of **22** was identical with an authentic sample. Mousseron, M.; Bousquet, H.; Marret, G. *Bull. Soc. Chim. Fr.* **1948**, 84.

THF under an argon atmosphere was slowly added *n*-butyllithium (0.64 mL, 1.3 M in hexane, 0.83 mmol). The reaction mixture was stirred for 15 min, after which time dry, distilled HMPA (0.32 mL, 1.9 mmol) was added, followed by freshly distilled benzenesulfonyl chloride (0.11 mL, 0.86 mmol). The resulting solution was stirred for 4 h at −78 °C and poured into water, and the mixture was extracted with ether. Concentration of the dried ($MgSO_4$) ether extract, followed by column chromatography (silica gel, eluted with 10% ethyl acetate in hexanes), gave 0.24 g (70%) of 3,3-bis(phenylthio)-1-propyl benzenesulfonate as a yellow oil: IR (film) 1480, 1450, 1440, 1360, 1185, 1095, 950, 910, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.10–2.16 (m, 2 H, CH_2CH_2O), 4.30 (t, J = 6.06 Hz, 2 H, CH_2O), 4.43 (t, J = 7.07 Hz, 1 H, $CH(SPh)_2$), 7.20–7.90 (m, 15 H, Ph); mass spectrum, (15 eV) m/e 416 (M^+) (2), 307 (5), 149 (100), 116 (27), 115 (13), 109 (18), 77 (25), 65 (11), 51 (14), 39 (9); high-resolution mass spectrum calcd for $C_{21}H_{20}O_3S_3$, m/e 416.0575; found, m/e 416.0602

3-Iodo-1,1-bis(phenylthio)propane. Sodium iodide (237 mg, 1.58 mmol) was added to a solution of 3.0 mL of 2-butanone containing 3,3-bis(phenylthio)-1-propyl benzenesulfonate (96.2 mg, 0.231 mmol) at 0 °C. The resulting mixture was stirred in the dark at 4 °C for 46 h, at which time the reaction was quenched by the addition of 5.0 mL of water, and the mixture was concentrated to remove the 2-butanone. Extraction of the residual material with ether followed by concentration of the dried ($MgSO_4$) extracts gave a yellow liquid which was purified by preparative layer chromatography (one silica gel plate eluted with 2% ethyl acetate in hexanes) to give 82 mg (92%) of 3-iodo-1,1-bis(phenylthio)propane as an unstable yellow oil: IR (film) 1580, 1475, 1465, 1430, 1210, 1010, 740, 680 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 2.10–2.40 (m, 2 H, CH_2), 3.35 (t, J = 7 Hz, 2 H, CH_2I), 4.40 (t, J = 6 Hz, 1 H, $CH(SPh)_2$), 7.10–7.60 (m, 10 H, Ph); mass spectrum, (15 eV) m/e 386 (M^+) (25), 277 (100), 149 (19); high-resolution mass spectrum calcd for $C_{15}H_{15}S_2I$, m/e 385.9668; found, m/e 385.9669.

1,1-Bis(phenylthio)-4,4-bis((*p*-*tert*-butylphenyl)thio)butane (9). *n*-Butyllithium (0.42 mL, 1.4 M in hexane, 0.60 mmol) was added to a solution of formaldehyde bis(*p*-*tert*-butylphenyl) thioacetal[30] (0.20 g, 0.60 mmol) in 5.0 mL of anhydrous THF at −23 °C under argon and the solution was stirred for 20 min. 3-Iodo-1,1-bis(phenylthio)propane (0.11 g, 0.29 mmol) in 1.5 mL of THF was added over a 10-min period, the solution was stirred for 30 min at −23 °C and added to 5.0 mL of water, and the mixture was extracted with ether. Concentration of the dried ($MgSO_4$) ether extract gave 0.48 g of crude material. Purification by preparative-scale HPLC (10-μm Licosorb, eluted with 2% ethyl acetate in hexanes) afforded 0.28 g (76%) of **9** as a yellow oil: IR (film) 2960, 1490, 1480, 1440, 1400, 1370, 830, 740, 690 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) 1.38 (s, 18 H, CH_3), 1.95–2.25 (m, 4 H, CH_2), 4.10–4.38 (m, 2 H, $CH(SPh)_2$ and $CH(SAr)_2$), 7.00–7.50 (m, 18 H, Ar and Ph); mass spectrum, (15 eV) m/e 602 (M^+) (2), 493 (9), 437 (100), 327 (64), 287 (13), 271 (32), 166 (21), 151 (27), 110 (23); high resolution mass spectrum calcd for $C_{30}H_{37}S_3$ (M^+ − SPh), m/e 493.2057; found, m/e 493.2046.

Cyclization of 1,1-Bis(phenylthio)-4,4-bis((*p*-*tert*-butylphenyl)thio)-butane (9). *sec*-Butyllithium (1.20 mL, 1.25 M in cyclohexane, 1.38 mmol) was added to a solution of TMEDA (0.26 mL, 1.7 mmol) and **9** (0.237 g, 0.394 mmol) in 6.0 mL of anhydrous THF at −78 °C under an argon atmosphere. The resulting yellow solution was stirred for 0.5 h at −78 °C at which time the dry ice–isopropyl alcohol bath was replaced by an ice bath. The solution was then stirred for an additional 0.5 h and poured into water, and the mixture was extracted with ether. Concentration of the dried ($MgSO_4$) extracts gave crude products which were purified by column chromatography (silica gel, eluted with 1% ethyl acetate in hexanes) to afford 0.0490 g of a yellow oil, homogeneous by silica gel TLC analysis but which proved to be a mixture of cyclobutenes: ^1H NMR (CCl_4) δ 1.33 (s, 66, CH_3), 2.56 (s, 20, CH_2), 7.10–7.60 (m, 66.2, Ar and Ph); mass spectrum, at 40 °C (15 eV) m/e 382 (1.5), 344 (8), 326 (100), 293 (15), 270 (17), 193 (17), 179 (11), 161 (6), 160 (6), 159 (6), 151 (16), 149 (12), 123 (6). Reverse-phase HPLC analysis (5-μm octadecylsilyl column, 4.6 × 230 mm, eluted with 5% methanol in water, flow rate 1.0 mL/min) including co-injection experiments, showed this oil to be a mixture of 1,2-bis(phenylthio)cyclobutene (**2A**), retention time 6.6 min, 1-(phenylthio)-2-((*p*-*tert*-butylphenyl)thio)-cyclobutene (**10**), retention time 11.6 min, and 1,2-bis((*p*-*tert*-butylphenyl)thio)cyclobutene (**11**), retention time 21.6 min, in a ratio of 12:81:7.

Preparation of 1,2-Bis(phenylthio)cyclobutene (2A) in the Presence of Lithium (*p*-*tert*-Butylphenyl)thiolate. *sec*-Butyllithium (10.5 mL, 1.09 M in cyclohexane, 11.4 mmol) was added to a solution of *p*-*tert*-butylthiophenol (0.752 g, 4.53 mmol), 1,1,4,4-tetrakis(phenylthio)butane (0.798 g, 1.63 mmol), and TMEDA (1.75 mL, 11.6 mmol) in 23.0 mL of THF at −78 °C under argon. The resulting solution was stirred for 20 min at −78 °C at which time the acetone–dry ice bath was replaced with an ice bath. After an additional 5 min the reaction was quenched by rapidly adding it to 50.0 mL of water. The mixture was concentrated, the residual material was extracted with ether, and the combined ether extracts were washed with 10% aqueous NaOH. Concentration of the dried ($MgSO_4$) extracts gave 0.756 g of a crude product mixture which was separated into two fractions by flash chromatography (silica gel, eluted with 2% ethyl acetate in hexanes). The first fraction consisted of 0.338 g of a yellow oil whose NMR and mass spectra were identical with those of an authentic sample of 1,2-bis(phenylthio)cyclobutene (**2A**). Further analysis of this fraction by RP-HPLC (5-μm octadecylsilyl column, eluted with 5% water in methanol) including co-injection experiments with samples of 1,2-bis((*p*-*tert*-butylphenyl)thio)cyclobutene (**11**) and a solution consisting of approximately 80% of 1-((*p*-*tert*-butylphenyl)thio)-2-(phenylthio)cyclobutene (**10**), from the ring closure of bis(diphenyl thioacetal) **9**, showed that no **10** or **11** was present. The slower moving fraction from the flash column gave 0.027 g of a white solid whose TLC, NMR, and mass spectra were identical with those of **1A**.

1,1,6,6-Tetrakis(phenylthio)hexane (1C). To a solution of bis(phenylthio)methane (1.4 g, 6.2 mmol) in 50 mL of anhydrous THF at −23 °C under argon was added *n*-butyllithium (4.5 mL, 1.38 M in hexane, 6.2 mmol) and the solution was stirred from 20 min. 1,4-Diiodobutane (0.40 mL, 3.0 mmol) was slowly added and the solution was stirred for an additional 0.5 h at −23 °C, added to water and the mixture extracted with ether. Concentration of the dried ($MgSO_4$) ether extract followed by recrystallization of the residue from acetonitrile afforded 1.3 g (84%) of bis(diphenyl thioacetal) **1C** as a white solid: mp 82–83 °C; IR (CCl_4) 1580, 1480, 1440 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.50–2.00 (m, 8 H, CH_2), 4.28 (t, J = 6 Hz, 2 H, $CH(SPh)_2$), 7.10–7.63 (m, 20 H, Ph); mass spectrum, (15 eV) m/e 518 (M^+) (0.68), 409 (12), 300 (7.5), 189 (100), 123 (15), 110 (19). Anal. Calcd for $C_{30}H_{30}S_4$: C, 69.49; H, 5.79; S, 24.70. Found: C, 69.51; H, 5.86; S, 25.00.

Cyclization of Bis(diphenyl thioacetal) 1C. Methyllithium (2.80 mL, 1.70 M in diethyl ether, 4.80 mmol) was added to a solution of **1C** (1.20 g, 2.31 mmol) and TMEDA (0.750 mL, 5.16 mmol) in 20 mL of THF at 0 °C under an argon atmosphere. The reaction mixture was stirred for 6 h at which time water was added. Rotary evaporation of the dried ($MgSO_4$) ether extract afforded 734 mg of a crude product mixture. Purification by MPLC (silica gel, eluted with 10% CCl_4 in hexanes) afforded 276 mg (40.0%) of **4** as a white solid: mp 106.0–107.5 °C; IR (CCl_4) 1580, 1480, 1440 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.45–1.80 (m, 4 H, $CHCH_2CH$), 1.99–2.10 (m, 2 H, $CHCH_2CH$), 2.284 (dd, J = 1.21, 5.05 Hz, 2 H, tertiary CH), 7.13–7.42 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) 25.721, 26.918, 27.662, 39.601, 125.597, 126.341, 128.088, 128.282, 128.735, 129.738, 136.202; mass spectrum, (15 eV) m/e 298 (M^+) (22), 189 (100), 155 (11), 114 (17); high-resolution mass spectrum calcd for $C_{18}H_{18}S$, m/e 298.0849; found, m/e 298.0838. In another experiment, run on a much larger scale, MPLC of the crude reaction product (silica gel, eluted with 1% ethyl acetate in hexanes followed by 5% benzene in hexanes) separated a slightly impure yellow oil from the more mobile (on silica gel) 6,6-bis(phenylthio)bicyclo[3.1.0]hexane (**4**). Further purification by preparative-scale HPLC (silica gel, eluted with 0.5% ethyl acetate in hexanes) afforded 1,2-bis(phenylthio)cyclohexene (**2C**) in less than 10% yield: IR (film) 1580, 1480, 1440 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 1.45–1.80 (m, 4 H, CH_2), 1.95–2.35 (m, 4 H, allylic CH_2), 7.05–7.40 (m, 10 H, Ph); high-resolution mass spectrum calcd for $C_{18}H_{18}S_2$, m/e 298.0849; found, m/e 298.0859.

6,6-Bis(phenylthio)bicyclo[3.1.0]hexane (4). The procedure was similar to that used by Braun and Seebach[4] for the preparation of the corresponding bicycloheptane except that methyllithium rather than butyllithium was used for the ring-closure step; we have noted that butyllithium causes significant sulfur–lithium exchange in the product. From 20.0 g (83.3 mmol) of bis(phenylthio)methane and 9.5 mL (113 mmol) of cyclopentene oxide was isolated 14.5 g (58%) of white crystals, mp 109–110 °C. The spectroscopic properties were identical with those for **4** produced by ring closure of **1A**.

Preparation and Ring Closure of 1,1,6,6-Tetrakis((*p*-*tert*-butylphenyl)thio)hexane. 1,1,6,6-Tetrakis((*p*-*tert*-butylphenyl)thio)hexane was prepared from bis((*p*-*tert*-butylphenyl)thio)methane[30] and 1,4-diiodobutane in the same manner that 1,1,6,6-tetrakis(phenylthio)hexane (**1C**) was prepared from bis(phenylthio)methane and 1,4-diiodobutane. Purification of the crude reaction mixture by MPLC (silica gel, eluted with 50% CCl_4 in hexanes followed by CCl_4) gave 53% of 1,1,6,6-tetrakis((*p*-*tert*-butylphenyl)thio)hexane as a white crystalline solid: mp 121–125 °C; IR (KBr) 2950, 2900, 2850, 1480, 1460, 1385, 1360, 1265, 1115, 1005, 825 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.33 (s, 36 H, CH_3), 1.43–1.97 (m, 8 H, CH_2), 4.20 (t, J = 6 Hz, 2 H, $CH(SAr)_2$), 7.15–7.50

(30) Uneyana, K.; Namba, N.; Oae, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1928.

(m, 16 H, Ar); mass spectrum, (15 eV) *m/e* 577 (M^+ – SAr) (10), 330 (19), 315 (9), 246 (25), 245 (100), 189 (34), 166 (28), 151 (48); high-resolution mass spectrum calcd for $C_{36}H_{49}S_3$ (M^+ – SAr), *m/e* 577.2996; found, *m/e* 577.2983. 6,6-Bis((*p-tert*-butylphenyl)thio)bicyclo[3.1.0]-hexane (**20**) was prepared from 1,1,6,6-tetrakis((*p-tert*-butylphenyl)-thio)hexane in the same manner as 6,6-bis(phenylthio)bicyclo[3.1.0]-hexane (**4**) was prepared from bis(diphenyl thioacetal) (**1C**). Purification of the crude product mixture by preparative-scale HPLC (10-μm Licosorb, eluted with 1% ethyl acetate in hexanes) provided an analytically pure sample of **20**: IR (KBr) 2950, 2900, 2850, 1480, 1460, 1385, 1360, 1265, 1115, 1005, 825 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.33 (s, 18 H, CH_3), 1.77–2.07 (m, 6 H, CH_2), 2.13–2.35 (m, 2 H, CH), 7.24 (s, 8 H, Ar).

Preparation of 6,6-Bis((*p-tert*-butylphenyl)thio)bicyclo[3.1.0]hexane (20) by the Method of Braun and Seebach. The title compound was prepared in 47% yield from bis((*p-tert*-butylphenyl)thio)methane[30] and cyclopentene oxide, again using methyllithium in the ring-closure step, in the same manner that 6,6-bis(phenylthio)bicyclo[3.1.0]hexane was prepared from bis(phenylthio)methane and cyclopentene oxide. An analytically pure sample of the desired product was obtained by preparative-scale HPLC (10-μm Licosorb, eluted with 1% ethyl acetate in hexanes) to give **20**, whose NMR spectrum was identical with that of the product isolated from the double ring closure of 1,1,6,6-tetrakis((*p-tert*-butylphenyl)thio)hexane.

Detection of the Dianion (12) of 1,1,6,6-Tetrakis(phenylthio)hexane. Quench with D_2O. *sec*-Butyllithium (0.72 mL, 1.09 M in cyclohexane, 0.78 mmol) was added to a solution of 1,1,6,6-tetrakis(phenylthio)hexane (**1C**) (0.19 g, 0.37 mmol) and TMEDA (0.25 mL, 1.6 mmol) in 8.0 mL of anhydrous THF under argon. The resulting solution was stirred for 1 h at −45 °C at which time D_2O (3.0 mL) was added. The resulting solution was concentrated to remove the THF and extracted with ether. Concentration of the dried ($MgSO_4$) extracts gave 0.16 g of a crystalline solid whose NMR integration indicated that the recovered bis(diphenyl thioacetal) was 80–85% d_2: ^1H NMR ($CDCl_3$, 60 MHz) δ 1.40–2.10 (m, 52), 4.13–4.40 (m, 1), 7.00–7.66 (m, 126).

Preparation of 6,6-Bis(phenylthio)bicyclo[3.1.0]hexane (4) from the Dianion (12) of 1,1,6,6-Tetrakis(phenylthio)hexane. *sec*-Butyllithium (2.50 mL, 2.85 mmol) was added to a solution of 1,1,6,6-tetrakis(phenylthio)hexane (**1C**) (0.725 g, 1.40 mmol) and TMEDA (1.00 mL, 5.96 mmol) in 13.0 mL of anhydrous THF at −45 °C under argon. The resulting solution was stirred for 1 h at −45 °C at which time the hexanol–dry ice bath was removed and replaced with an ice bath. Stirring under argon was continued for another 6 h at which time the reaction was quenched by the addition of water. Extraction of the reaction mixture with ether followed by drying ($MgSO_4$) and concentration in vacuo afforded a crude product mixture. Purification by MPLC (silica gel, eluted with 1% ethyl acetate in hexanes) gave 0.201 g (48.1%) of a white crystalline substance whose ^1H NMR spectrum was identical with that of **4**.

Preparation of 1,1,1,6,6,6-Hexakis(phenylthio)hexane (13). *sec*-Butyllithium (3.50 mL, 1.15 M in cyclohexane, 4.03 mmol) was added to a solution of 1,1,6,6-tetrakis(phenylthio)hexane (**1C**) (1.00 g, 1.93 mmol) and TMEDA (1.30 mL, 8.61 mmol) in 40.0 mL of THF at −45 °C (hexanol–dry ice) under argon. After stirring for 1 h, phenyl benzenethiosulfonate (1.01 g, 4.04 mmol) was added and stirring was continued for an additional 45 min before the reaction was quenched with 10 mL of a 10% aqueous NH_4Cl solution. Upon concentration of the reaction mixture, a white precipitate formed and remained even after the addition of a small amount of ether. The solution was filtered to collect the crystalline substance. The mother liquor was concentrated to give another crop of crystals which were washed with 20 mL of ether and collected by filtration. A total of 0.876 g (61.8%) of **13** was collected as a white crystalline solid: mp 168.5–175.0 °C dec; IR (KBr) 1470, 1435, 1300, 1160, 1070, 1020, 920, 775, 750, 700, 685 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 1.60 (br s, 8 H, CH_2), 7.10–7.80 (m, 30 H, Ph); mass spectrum, (15 eV) *m/e* 514 (M^+ – 2(HSPh)) (1.5), 357 (100), 110 (47); high-resolution mass spectrum calcd for $C_{30}H_{26}S_4$ (M^+ – 2(HSPh)), *m/e* 514.0917; found, *m/e* 514.0912.

Conversion of 1,1,1,6,6,6-Hexakis(phenylthio)hexane (13) to 1,1,6,6-Tetrakis(phenylthio)hexane (1C). *sec*-Butyllithium (0.25 mL, 1.15 M in cyclohexane, 0.29 mmol) was added to a solution of (**13**) (98 mg, 0.13 mmol) in 5.0 mL of anhydrous THF at −45 °C (hexanol–dry ice) under argon. After 1 h the reaction was quenched with water and the resulting solution was extracted with ether. Concentration of the dried ($MgSO_4$) extract and separation of the crude product mixture by preparative layer chromatography (silica gel plate, eluted with 3% ethyl acetate in hexanes) afforded 39.6 mg (89.7%) of the expected *sec*-butylphenyl sulfide as the least polar product: ^1H NMR ($CDCl_3$, 90 MHz) δ 1.00 (t, *J* = 7 Hz, 3 H, CH_3CH_2), 1.25 (d, *J* = 7 Hz, CH_3CH), 1.33–1.87 (m, 2 H, CH_2), 2.87–3.63 (m, 1 H, CH), 7.10–7.57 (m, 5 H, Ph) and 66.3 mg (96.2%) of a white solid whose ^1H NMR spectrum is identical with that of **1C**.

Preparation of 6,6-Bis(phenylthio)bicyclo[3.1.0]hexane (4) from 1,1,1,6,6,6-Hexakis(phenylthio)hexane (13). *sec*-Butyllithium (1.20 mL, 1.15 M in cyclohexane, 1.38 mmol) was added to a solution of **13** (487 mg, 0.663 mmol) in 25.0 mL of THF at −45 °C (hexanol–dry ice) under argon. The resulting solution was stirred for 1 h at −45 °C at which time the hexanol–dry ice bath was substituted by an ice bath. The solution was stirred for an additional 5 h at 0 °C after which time water was added. The reaction mixture was concentrated to remove the THF and extracted with ether. Concentration of the dried ($MgSO_4$) extracts gave the crude product mixture which was subjected to column chromatography (30 g of silica, eluted with hexanes followed by 2% ethyl acetate in hexanes) to remove the *sec*-butylphenyl sulfide. Complete separation of the desired product was obtained by MPLC (silica gel, eluted with 10% benzene in hexanes) to give 69.1 mg (34.9%) of white crystalline solid whose ^1H NMR was identical with that of **4**.

5,5-Bis(phenylthio)-1-pentanol (21). Dry HCl was passed through a solution of 2,3-dihydropyran (0.92 mL, 10 mmol) in thiophenol (4.50 mL, 44 mmol) for 8 h at room temperature. The mixture was then stirred for an additional 14 h at ambient temperature and dissolved in ether, and the excess thiophenol was removed by washing the ether layer with 10% aqueous NaOH. Rotary evaporation of the dried ($MgSO_4$) ether layer gave the crude product. Purification by column chromatography (silica gel, eluted with 20% ethyl acetate in hexanes) afforded 3.04 g (96.5%) of 5,5-bis(phenylthio)-1-pentanol (**21**): IR (film) 3600–3100 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.00–2.10 (m, 6 H, CH_2), 2.50 (br s, 1 H, OH), 3.50 (t, *J* = 6 Hz, 2 H, CH_2O), 4.30 (t, *J* = 6 Hz, 1 H, $CH(SPh)_2$), 7.10–7.60 (m, 10 H, Ph); mass spectrum, (15 eV) *m/e* 304 (M^+) (5), 195 (68), 194 (36), 110 (9), 85 (100); high-resolution mass spectrum calcd for $C_{17}H_{20}OS_2$, *m/e* 304.0956; found, *m/e* 304.0956.

5,5-Bis(phenylthio)-1-pentyl Benzenesulfonate. *n*-Butyllithium (5.35 mL, 1.30 M in hexane, 6.95 mmol) was added to a solution of **21** (2.10 g, 6.91 mmol) in 100 mL of THF at −78 °C under argon. After the solution had been stirred for 20 min at −78 °C, anhydrous HMPA (2.50 mL, 14.4 mmol) was added to the yellow solution followed by freshly distilled benzenesulfonyl chloride (0.90 mL, 7.0 mmol). After having been stirred for 3 h at −78 °C, the reaction mixture was poured into water and extracted with ether. Concentration of the dried ($MgSO_4$) extracts gave 2.98 g of crude material, which, after purification by column chromatography (300 g of silica gel, eluted with 10% ethyl acetate in hexanes), gave 2.6 g (83%) of 5,5-bis(phenylthio)-1-pentyl benzenesulfonate: IR (film) 1475, 1440, 1430, 1355, 1185, 1170, 1090, 1020, 930, 730, 680 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.30–2.00 (m, 6 H, CH_2), 3.95 (t, *J* = 6 Hz, 2 H, CH_2OSO_2), 4.30 (t, *J* = 6 Hz, 1 H, $CH(SPh)_2$), 6.90–8.00 (m, 15 H, Ph); mass spectrum, (15 eV) *m/e* 334 (M^+ – SPh) (0.5), 177 (10), 110 (100); high-resolution mass spectrum calcd for $C_{17}H_{18}O_3$ (M^+ – SPh), *m/e* 334.0697; found, *m/e* 334.0693.

5-Iodo-1,1-bis(phenylthio)pentane. To 5,5-bis(phenylthio)-1-pentyl benzenesulfonate (1.13 g, 2.55 mmol) in 85.0 mL of 2-butanone was added an excess of sodium iodide (1.98 g, 13.2 mmol). The resulting solution was stirred in the dark for 40 h at 4 °C, at which time water was added and the mixture was concentrated by removal of the 2-butanone in vacuo. Extraction of the residual material with ether followed by concentration of the dried ($MgSO_4$) ether layer gave 0.938 g of crude material. Purification by preparative layer chromatography (3 silica plates, eluted with 2% ethyl acetate in hexanes) gave 0.735 g (69.6%) of 5-iodo-1,1-bis(phenylthio)pentane: IR (film) 2940, 1580, 1480, 1435, 1100, 740, 680 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.40–2.00 (m, 6 H, CH_2), 3.00 (t, *J* = 6 Hz, 2 H, CH_2I), 4.30 (t, *J* = 6 Hz, 1 H, $CH(SPh)_2$), 7.00–7.70 (m, 10 H, Ph); mass spectrum, (15 eV) *m/e* 414 (M^+) (4), 305 (100), 218 (20), 179 (25), 177 (25), 149 (16), 123 (37), 110 (21), 69 (33); high-resolution mass spectrum calcd for $C_{11}H_{14}SI$ (M^+ – SPh), *m/e* 304.9861; found, *m/e* 304.9861.

1,1-Bis(phenylthio)-6,6-bis((*p-tert*-butylphenyl)thio)hexane (19). *n*-Butyllithium (2.5 mL, 1.4 M in hexane, 3.5 mmol) was added to a solution of bis((*p-tert*-butylphenyl)thio)methane (1.2 g, 3.5 mmol) in 20 mL of anhydrous THF at −23 °C under argon. After the resulting solution had been stirred for 20 min, 5-iodo-1,1-bis(phenylthio)pentane (1.31 g, 3.16 mmol) in 8.0 mL of THF was added. The mixture was stirred for 20 min at −23 °C, poured into water, and extracted with ether. Concentration of the dried ($MgSO_4$) ether extracts and purification by column chromatography (silica gel, eluted with 1% ethyl acetate in hexanes) afforded 1.8 g of a slightly impure yellow oil. Further purification by preparative-scale HPLC (10 μm Licosorb, eluted with 1% ethyl acetate in hexanes) gave 0.83 g (41%) of **19** as a very viscous yellow oil: IR (film) 2990, 2925, 2890, 1595, 1490, 1450, 1410, 1380, 1290, 1140, 1050, 1040, 850, 805, 780, 710 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.33 (s, 18 H, CH_3), 1.40–2.07 (m, 8 H, CH_2), 4.07-4.40 (m, 2 H, $CH(SAr)_2$ and $CH(SPh)_2$), 7.07–7.53 (m, 18 H, Ar and Ph); mass spectrum, (15 eV) *m/e* 630 (M^+) (4), 465 (29), 357 (11), 299 (13), 245 (33), 189

(100), 166 (12), 151 (15), 110 (15); high-resolution mass spectrum calcd for $C_{38}H_{46}S_4$, m/e 630.2482; found, m/e 630.2465.

Cyclization of 1,1-Bis(phenylthio)-6,6-bis((*p*-*tert*-butylphenyl)thio)-hexane (19). To a solution of **19** (0.770 g, 1.22 mmol) and TMEDA (0.41 mL, 2.7 mmol) in 11.0 mL of anhydrous THF at 0 °C under argon was added methyllithium (1.65 mL, 1.55 M in diethyl ether, 2.56 mmol). The resulting solution was stirred for 6 h at 4 °C, at which time water was added and the resulting solution was extracted with ether. Concentration of the dried ($MgSO_4$) ether extract followed by purification by column chromatography (silica gel, eluted with 1% ethyl acetate in hexanes) afforded 0.46 g of an impure mixture of bicyclo[3.1.0]hexanes. Analysis of this crude mixture by RP-HPLC (5-μm octadecylsilyl column, 4.6 × 250 mm, eluted with 3% water in methanol, flow rate 1.0 mL/min) including co-injection experiments showed that the only bicyclic compounds formed were 6,6-bis(phenylthio)bicyclo[3.1.0]hexane (**4**), retention time 7.19 min, and 6,6-bis(*p*-*tert*-butylphenylthio)bicyclo-[3.1.0]hexane (**20**), retention time 17.8 min.

Detection of the Dianion (22) of 5,5-Bis(phenylthio)-1-pentanol. Quench with D_2O. *sec*-Butyllithium (0.75 mL, 1.1 M in cyclohexane, 0.82 mmol) was added to a solution of 5,5-bis(phenylthio)-1-pentanol (**21**) (0.119 g, 0.391 mmol) in 4.8 mL of anhydrous THF at −78 °C under argon. The resulting solution was stirred for 1 h at −78 °C at which time 2.0 mL of D_2O was added. The reaction mixture was extracted with ether, and the combined extracts were dried ($MgSO_4$), filtered, and concentrated. Purification by column chromatography (1 g of silica gel, eluted with hexanes followed by 20% ethyl acetate in hexanes) to remove a small amount of nonpolar impurities gave 0.080 g of a yellow oil whose NMR spectrum indicated that the recovered **21** was more than 93% deuterated at the thioacetal carbon atom: ^1H NMR (CCl_4, 90 MHz) δ 1.10–2.03 (m, 105, CH_2), 2.13 (br s, 16, OH), 3.53 (t, J = 7 Hz, 28, CH_2O), 4.37 (t, J = 6 Hz, 1, $CH(SPh)_2$), 7.13–7.67 (m, 139, Ph).

Cyclization of 5,5-Bis(phenylthio)-1-pentanol (21). *sec*-Butyllithium (4.10 mL, 1.09 M in cyclohexane, 4.47 mmol) was added to a solution of **21** (0.643 g, 2.11 mmol) and TMEDA (0.70 mL, 4.6 mmol) in 26.0 mL of anhydrous THF at −78 °C under argon. The resulting solution was stirred for 1 h at −78 °C and then at 4 °C for 20 h. The reaction was quenched by addition to 25.0 mL of a 10% aqueous NH_4Cl solution. The reaction mixture was concentrated by removal of the THF in vacuo and extracted with ether. Concentration of the dried ($MgSO_4$) extracts gave 0.672 g of crude products. Purification by column chromatography (60 g of silica gel, eluted with 10% ethyl acetate in hexanes followed by 20% ethyl acetate in hexanes) gave a first fraction of 0.0886 g (21.6%) of *cis*-2-(phenylthio)cyclopentanol: IR (film) 3650–3200 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.54–2.13 (m, 6 H, CH_2), 2.65 (br s, 1 H, OH) 3.41–3.49 (m, 1 H, C*H*SPh), 4.09 (t, J = 3.5 Hz, 1 H, CHO), 7.20–7.50 (m, 5 H, Ph); mass spectrum, (15 eV) m/e 194(M^+) (100), 166 (15), 110 (86), 85 (12), 84 (28), 67 (14); high-resolution mass spectrum calcd for $C_{11}H_{14}OS$, m/e 194.0765; found, m/e 194.0765. The slower moving component consisted of 0.056 g (13.8%) of *trans*-2-(phenylthio)cyclopentanol whose 300-MHz ^1H NMR was idential with that of an authentic sample:[29] IR (film) 3650–3125 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.54–1.88 and 2.00–2.31 (m, 7 H, CH_2 and OH), 3.36–3.43 (m, 1 H, C*H*SPh), 4.102 (m, 1 H, CHO), 7.16–7.43 (m, 5 H, Ph); mass spectrum, (15 eV) m/e 194 (M^+) (100), 166 (14), 110 (92), 84 (40), 83 (10), 67 (14); high-resolution mass spectrum calcd for $C_{11}H_{14}OS$, m/e 194.0765; found, m/e 194.0765.

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Hydroboration Kinetics. 6.[1] Hydroboration of Alkenes with 9-Borabicyclo[3.3.1]nonane Dimer and 9-Borabicyclo[3.3.1]nonane–Lewis Base Complexes in Various Solvents: An Interpretation of the Catalytic Effect of Ether Solvents on the Hydroboration Reaction

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Abstract: The hydroboration of alkenes with 9-borabicyclo[3.3.1]nonane dimer in noncomplexing solvents such as carbon tetrachloride, benzene, and cyclohexane and possible complexing solvents such as tetrahydrofuran, 2,5-dimethyltetrahydrofuran, and dimethyl sulfide and with 9-borabicyclo[3.3.1]nonane–amine complexes (pyridine, 2-methylpyridine, trimethylamine, and *N*-methylpiperidine) has been examined. These results provide an insight into the role of the complexing solvent on the hydroboration reaction. It is proposed that the complexing agent is not directly involved in the actual hydroboration step but provides an alternative lower energy pathway to monomeric boranes. This interpretation provides a reasonable explanation for the marked catalytic effect of ethers and weakly basic amines on the rate of hydroboration with diborane, a phenomenon previously not accounted for. This catalytic effect may well be a special example of a general phenomenon in reactions of associated organometallics.

The discovery of the enormous catalytic effect of ethers on the hydroboration of alkenes with diborane $(BH_3)_2$ more than two decades ago[3] marked the beginning of a rapid expansion of organoborane chemistry.[4] The reaction of an unhindered alkene with diborane is essentially instantaneous in ether solvents,[5] in sharp contrast with the extreme slowness of the reaction in the gas phase[6] and in hydrocarbon solvents (eq 1).[3c] Despite many

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