oil which contained a single volatile product by GLC analysis (5 ft × 0.25 in. QF-1 column, 150 °C). Analysis of this residue by ^1H NMR indicated that **20** was obtained in ca. 85% yield. Kugelrohr distillation of this oil gave 212 mg (66% yield) of **20**: ^1H NMR δ ($CDCl_3$) 3.2 (s, 3 H, $-OCH_3$), 2.23–2.11 (m, 2 H, bridgehead protons), 1.84 (s, 4 H, CH_2CH_2), 1.86–1.70 (m, 8 H, methylene protons at C-2, C-7, C-10, and C-11), 1.60 (br s, 1 H, OH), 1.49 (br t, 2 H, CH_2 at C-9); ^{13}C NMR δ ($CDCl_3$) 75.8 (C-6), 72.4 (C-3), 48.2 (CH_3), 46.4 (C-2 and C-11), 42.3 (C-7 and C-10), 37.9 (C-4), 35.1 (C-5), 32.6 (C-9), 29.1 (C-1 and C-8); IR ν (CCl_4): 2925, 2860, 1520, 1040, 985 cm^{-1}; exact mass calcd for $C_{12}H_{20}O_2$, 196.146; found, 196.147.

3,6-Dimethoxyhomoadamantane (21). Methylation of **20** (212 mg, 1.08 mmol) with sodium hydride (450 mg, 18.8 mmol) and methyl iodide (0.6 mL) in dry THF by the procedure described for **12** → **19** provided an oil which was Kugelrohr distilled to afford 95 mg (42% yield) of **21** as a clear oil: ^1H NMR δ ($CDCl_3$) 3.20 (s, 6 H, OCH_3), 2.25–2.13 (br m, 2 H, bridgehead protons), 1.85 (s, 4 H, CH_2CH_2), 1.89–1.63 (m, 8 H, methylene protons at C-2, C-7, C-10, and C-11), 1.48 (br t, 2 H, CH_2 at C-9); ^{13}C NMR δ ($CDCl_3$) 76.0 (C-3 and C-6), 48.1 (CH_3), 42.3 (C-2, C-7, C-10, and C-11), 35.3 (C-9), 32.6 (C-4 and C-5), 28.8 (C-1 and C-8); IR ν (CCl_4) 2940, 2850, 2820, 1450, 1370, 1260, 1150, 1085 cm^{-1}; exact mass calcd for $C_{13}H_{22}O_2$, 210.162; found, 210.162.

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55. Found: C, 74.48; H, 10.77.

1-Methoxyhomoadamantane[29] **(25).** Methylation of **14** (90 mg, 0.54 mmol) with sodium hydride (100 mg, 4.20 mmol) and methyl iodide (0.6 mL) in dry THF by the procedure described for **12** → **19** provided an oil which was Kugelrohr distilled to give 87 mg (89% yield) of **25**: ^{13}C NMR δ ($CDCl_3$) 72.7 (C-1), 47.9 (CH_3), 41.2 (C-2 and C-10), 40.7 (C-9), 37.3 (C-7 and C-11), 33.0 (C-4 and C-5), 31.5 (C-3 and C-6), 31.4 (C-8).

1-Methoxyhomoadamantan-3-ol (26). According to the general procedure described for **7** → **13**, a stream of ozone in oxygen was passed for 2.5 h through a mixture of **25** (87 mg, 0.44 mmol) adsorbed on silica gel (10 g) that was maintained at −78 °C. This material was then allowed to slowly warm to room temperature and the silica gel was eluted with ethyl acetate (750 mL). Evaporation of the solvent at reduced pressure provided an oil which contained a single volatile product by GLC analysis (5 ft × 0.25 in. QF-1 column, 150 °C). Kugelrohr distillation of this oil provided 84 mg (89% yield) of **26**: ^1H NMR δ ($CDCl_3$) 3.24 (s, 3 H, OCH_3), 2.32–2.14 (m, 2 H, bridgehead protons), 2.07–1.43 (m, 15 H); ^{13}C NMR δ ($CDCl_3$) 73.4 (C-1), 72.6 (C-3), 50.1 (C-2), 48.2 (OCH_3), 46.4 (CH_2), 41.3 (CH_2, double intensity), 40.0 (CH_2), 36.6 (CH_2), 31.3 (CH), 29.8 (CH), 29.5 (CH_2); exact mass calcd for $C_{12}H_{20}O_2$, 196.146; found, 196.146.

Acknowledgment. This work was supported by grants from the United Parkinson Foundation and the University of Delaware Research Foundation.

Registry No. **7**, 281-46-9; **8**, 14504-84-8; **9**, 14651-42-4; **12**, 14504-80-4; **13**, 87350-97-8; **14**, 31061-64-0; **15**, 24669-56-5; **16**, 770-71-8; **17**, 21898-96-4; **19**, 21898-92-0; **20**, 87350-98-9; **21**, 87350-99-0; **25**, 21898-95-3; **26**, 87351-00-6; CrO_3, 1333-82-0; lead tetraacetate, 546-67-8; *p*-nitroperbenzoic acid, 943-39-5.

Stereochemistry of the Reactions of Lithium Di-*tert*-butylbiphenyl with Alkyl Halides

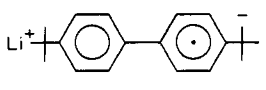
Peter K. Freeman* and Larry L. Hutchinson

Department of Chemistry, Oregon State University, Corvallis, Oregon 97330-4003

Received March 15, 1983

The stereochemistry of the reaction of lithium di-*tert*-butylbiphenyl with cyclopropyl halides, 7-chloronorcarane, 7-bromo-7-methylnorcarane, and *anti*-3-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane generated syn/anti lithio reagent ratios of 1:10, 3:1, and 200:1, respectively. Similar treatment of noncyclopropyl secondary halides *syn*-7-bromonorbornene, *anti*-7-bromobenzonorbornadiene, *exo*-2-chloronorbornane, and 4-chloro-*tert*-butylcyclohexane resulted in lithio reagent ratios of 1:3.8 (syn/anti), 1:1.33 (syn/anti), 10:1 (exo/endo), and 1:14 (cis/trans), respectively. For the cyclopropyl radicals generated in the first group, the lithio reagent ratios describe the related radical equilibrium; the significance of the stereochemistry of the reaction of LiDBB with noncyclopropyl secondary halides is discussed in terms of both precursor radicals and carbanions.

A study of the stereochemistry of the reaction of the newly developed lithium *p,p*′-di-*tert*-butylbiphenyl (LiDBB,[1] **1**) with alkyl halides is of interest for two reasons.



1 (LiDBB)

The mechanistic features revealed provide information about the reactions of a sterically hindered aromatic radical anion with alkyl halides and allow one to view the configurational equilibria of radicals and anions, the latter opportunity provided more easily and with fewer ambiguities than with other chemical methods. Second, the stereochemistry of the organolithium product is of considerable synthetic importance, and our study provides some useful guidelines.

Reactions with Cyclopropyl Halides

Cyclopropyl radicals are highly pyramidal and hold their configuration for on the order of 10^{-8}–10^{-10} s.[2-4] This is far longer than the time of a single collision between molecules in solution and is even longer than the time of an encounter. (An encounter is thought to consist of a number of collisions and lasts around 10^{-11} s.)[5] Thus, it is clear that any reaction which is diffusion controlled and reacts with retention of configuration to give stable products would be capable of accurately giving the equilibrium population of radicals. The expectation that LiDBB would react with cyclopropyl radicals at diffusion-controlled rates seems most reasonable. It is generally accepted that cyclopropyl radicals are highly unstable

---

(1) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 1924.

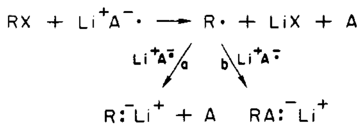
(2) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(3) Kawamura, T.; Tsumura, M.; Yokomichi, Y.; Yonezawa, T. *J. Am. Chem. Soc.* **1977**, *99*, 8251.

(4) Dupuis, M.; Pacansky, J. *J. Chem. Phys.* **1982**, *76*, 2511.

(5) Jordan, P. C. "Chemical Kinetics and Transport"; Plenum Press: New York, 1979; p 309.

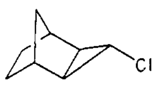
Scheme I[a]



[a] A = aromatic substrate.

(reactive) while cyclopropyl anions are relatively stable, in comparison to primary systems.[6] It would be expected, then, that the electron affinity of a cyclopropyl radical is higher than that of a primary radical. The electron affinity of *p,p'*-di-*tert*-butylbiphenyl (DBB) is 0.16 V lower than that of naphthalene.[7,8] Since the rate of electron transfer is expected to be dependent upon the difference of electron affinities, it is clear that cyclopropyl radicals can be expected to react with DBB· faster than primary radicals react with naphthalenide. Thus, it appears to be likely that cyclopropyl radicals will react with LiDBB at least as fast as primary radicals react with sodium naphthalenide,[9] which is known to be diffusion rate controlled.[10] The stability of the products is also well established. It has been demonstrated that cyclopropyllithium reagents are quite stable even under adverse conditions.[11-14] Even the free cyclopropyl anion would be expected to be stable at −78 °C.[15]

In our earlier study of the radical equilibrium set up by dissociative one-electron transfer to *anti*-3-chlorotricyclo[3.2.1.0^{2,4}]octane (*anti*-2-Cl) we found lithium–naphthalene radical anion to be a satisfactory reagent to determine the relative population of *syn*- and *anti*-cyclopropyl radical species;[11] however, the superior yields of alkyllithium product with minimal alkylation of the radical anion (predominance of route a over b in Scheme I) that we have observed with LiDBB and the advantage in driving force for electron transfer suggest that LiDBB is the reagent which deserves the focus of our attention.



anti-2-Cl

7-Norcaranyl System (3). The reaction of a mixture of *syn*- and *anti*-7-chloronorcarane (syn/anti ratio of 1.5) with LiDBB in THF at −78 °C followed by quenching with deuterium oxide gave 3-*D*. NMR analysis indicated the anti/syn ratio to be 5:1. However, the analysis of this compound by NMR was plagued by the presence of even very small amounts of impurities whenever the anti to syn ratio is very large or very small. For this reason, the deuteration experiment only gives the direction and approximate magnitude of the configuration of the lithium reagents. Due to the unsatisfactory NMR analysis, a better method of determining the lithium reagent populations was required. It appears well-established that metal–halogen exchange between alkyllithium reagents and ethylene dibromide goes with retention of configuration.[16] To show that ethylene dibromide could be used as a suitable quencher of the lithium reagents, *syn*- and *anti*-3-Li were prepared separately by metal–halogen exchange of *syn*- and *anti*-3-Br, and the resultant lithium reagents were quenched both with deuterium oxide and with ethylene dibromide (Scheme II). Retention was observed in all cases. This demonstration of retention of configuration is not sufficient in itself to allow ethylene dibromide to be used to determine lithium reagent ratios. It must also be shown that the yields from the two forms are the same. To this end, a mixture of 7-bromonorcaranes (anti/syn ratio of 1.33) was treated in the same manner just described but with the inclusion of an internal standard. The overall yield for the *anti*-bromide was 92%, with the *syn*-bromide giving an 84% yield (final anti/syn ratio of 1.45). Repetition of this procedure with deuterium oxide as the quench gave an anti to syn deuteration ratio of 1.39. Thus, either deuterium oxide or ethylene dibromide should be suitable to determine the anti/syn ratio of 3-Li.

Scheme II

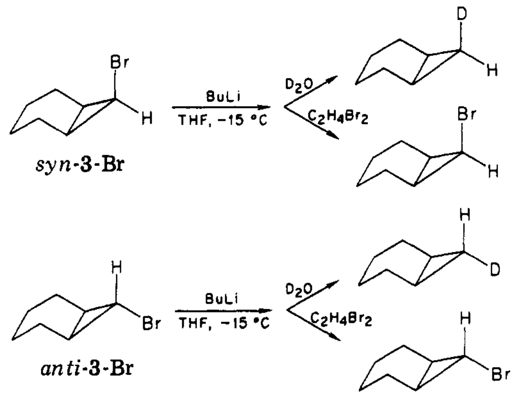
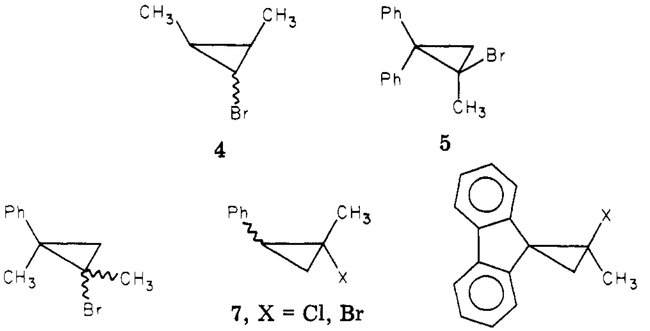


Chart I



4

5

6

7, X = Cl, Br

8, X = Cl, Br

From a reinvestigation of the reaction of LiDBB with the 1.5:1 mixture of *syn*- and *anti*-3-Cl using ethylene dibromide as the quench, it was found that the anti to syn ratio of bromides was 10 ± 2 (estimated error). In contrast to our results with 2[11] and the lithium naphthalenide reductions of *cis*- and *trans*-4,[17] Jacobus and Pensak found that sodium naphthalenide reduction of optically active

---

[6] Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625. Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516. Buncel, E. "Carbanions: Mechanistic and Isotopic Aspects"; Elsevier: Amsterdam, 1975; Chapter 1.

[7] Evans, A. G.; Jerome, B.; Rees, N. H. *J. Chem. Soc., Perkin Trans. 2* 447 (1973).

[8] Curtis, M. D.; Allred, A. L. *J. Am. Chem. Soc.* **1965**, *87*, 2554.

[9] Lithium naphthalenide and sodium naphthalenide, both as loose ion pairs, react in electron-exchange reactions with naphthalene in THF at virtually the same rate (1.3–1.7 × 10^9 and 1.0 × 10^9 M^{-1} s^{-1}, respectively). Szwarc, M. "Ions and Ion pairs in Organic Rections"; Wiley: New York, 1974; Vol. 2, p 57.

[10] Garst, J. F.; Barton, F. E., II. *Tetrahedron Lett.* **1969**, 587.

[11] Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 3191. Freeman, P. K.; Hutchinson, L. L.; Blazevich, J. N. *Ibid.* **1974**, *39*, 3606.

[12] Walborsky, H. M.; Arnoff, M. S. *J. Organomet. Chem.* **1973**, *51*, 55.

[13] Dewar, M. J. S.; Harris, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 3652.

[14] Walborsky, H. M.; Impastato, F. J.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3283.

[15] Carter, R. E.; Drakenberg, T.; Bergman, N. A. *J. Am. Chem. Soc.* **1975**, *97*, 6990.

[16] Glaze, W. H.; Selman, C. M.; Ball, A. L., Jr.; Bray, L. E. *J. Org. Chem.* **1969**, *34*, 641.

[17] Boche, G.; Schneider, D. R. *Tetrahedron Lett.* **1978**, 2327.

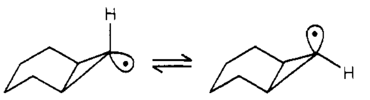
[18] Jacobus, J.; Pensak, D. *J. Chem. Soc. D* **1969**, 400.

Table I. Reaction of *anti*-**9**-Br with LiDBB in THF

addition mode	concn,[a] M	retention/ inversion,[b]	% anion trapping[c]
normal	0.029	0.377	94
normal	0.17	0.356	95
evaporative	0.30	0.398	
inverse	0.01	0.426	95

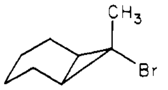
[a] Concentration of pot solution-electron donor in all but inverse addition. The temperature was −78 °C in all cases. [b] *anti*-9-H/*syn*-9-H ratio. [c] By CO_2 quench method.

5 (Chart I) proceeds with 29% retention of optical activity.[18] Recently, Boche, in a study of naphthalenide reduction of *cis*- and *trans*-**6**[17] and *cis*- and *trans*-**7**, observed identical hydrocarbon ratios irrespective of the geometry of the cyclopropyl halide starting material, while naphthalenide reduction of optically active **8** proceeds with net retention. These results are the basis for the suggestion that the net retention observed for **5** by Jacobus and Pensak is due to formation of a radical anion with the additional electron associated with the phenyl substituents. The radical anion so formed provides an opportunity for subsequent intramolecular trapping of cyclopropyl radical or a closely related variation of this.[19] Since the 7-norcaranyl system is free of the complications associated with the presence of an aromatic electron acceptor, the standard mechanism is anticipated with the generation of free cyclopropyl radicals (Scheme I). Proton tunneling of the radicals derived from **3**-Cl would be expected to cause more rapid interconversion than with those related to **6** and **7** and at a rate too rapid to allow the first-formed configuration to be trapped by 0.15 M LiDBB, even at −78 °C. This is, in fact, the case. Purified *syn*- and *anti*-**3**-Cl were separately subjected to the above procedure with the result that the anti to syn ratio of bromides was 11:1 in each case. These results indicate that the anti radical is more stable than the syn as illustrated in eq 1.



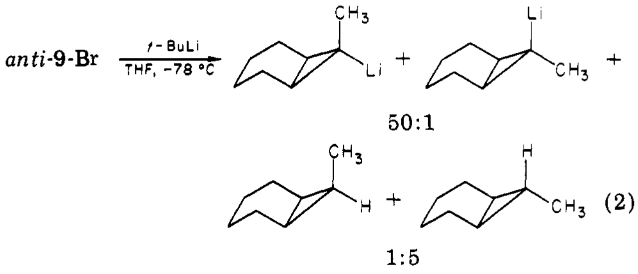
10:1 (1)

7-Methylnorcaranyl System (9). This system is of interest not only for determination of the effect of methyl on the position of the radical equilibrium but also since it might be possible to trap the radical before complete equilibration can occur. This was considered to be a possibility in this case since the fast proton tunneling expected with the norcaranyl radical is absent in this system. It was also hoped, at the time of the experiment, that running the reaction at a low temperature would lower the rate of inversion and result in more trapping than we believed Jacobus and Pensak had observed with the 2,2-diphenyl-1-methylcyclopropyl radical at 20 °C.



anti-9-Br

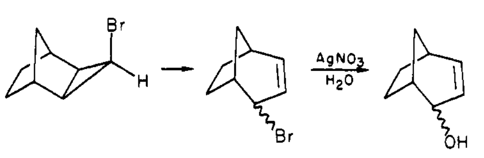
Stereochemical data for the products from the reaction of *anti*-**9**-Br with LiDBB under a variety of conditions are presented in Table I. The method of carbon dioxide quenching was used to determine the extent of lithium incorporation as it should be valid for LiDBB reactions.[1] As can be seen from the four entries of Table I, increasing the concentration of radical anion does not increase the ratio of retention to inversion; the opposite trend (if any) is observed. Although increasing viscosity with increasing radical anion concentration may be responsible for the 20% range observed, it seems more likely that errors may have accumulated in the workup. As a check on the stereochemistry of the product hydrocarbons (originally assigned by comparing the products from water and ethylene dibromide quenches of **9**-Li formed from LiDBB treatment of *anti*-**9**-Br), *anti*-**9**-Br was allowed to undergo exchange with *tert*-butyllithium at −78 °C for 5 min in THF (eq 2). Analysis by gas chromatography of an aliquot



(2)

quenched in water and of the remainder after treatment with carbon dioxide revealed that, while a 53% yield of lithium reagent was obtained, a 33% yield of hydrocarbons was simultaneously produced. The lithium reagent was produced largely (50:1) with retention of configuration, the hydrocarbons derived from the alkyllithium species corresponding to the original stereochemical assignment. The hydrocarbon side products of the exchange reaction were of essentially inverted configuration, with the major hydrocarbon having the configuration of the more stable radical as determined from LiDBB experiments.

***exo*-Tricyclo[3.2.1.0^{2,4}]octyl System (2).** The stereochemistry of the reaction of *anti*-**2**-Cl with lithium naphthalene followed by deuterium oxide to give at least a 100:1 syn/anti deuteration ratio has been described previously.[11] To complete our analysis of the reaction of cyclopropyl halides with LiDBB, we treated *anti*-**2**-Cl with LiDBB at −78 °C and NMR analysis of the hydrogens at C-3 following deuterolysis gave an identical result to that obtained with lithium naphthalene (>100:1 syn/anti deuterium incorporation). With the goal of obtaining a more precise value for the syn to anti ratio in the LiDBB case, we repeated the reaction using ethylene dibromide as the quench. The syn bromide is known to spontaneously decompose[20] as shown (first part of eq 3). Treatment



(3)

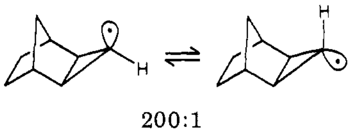
of the reaction mixture with aqueous silver nitrate removed the allylic bromide (eq 3). Gas chromatographic analysis showed only one product component, *anti*-**2**-Br. From the integration of this peak relative to the internal standard, it was concluded that the *anti*-bromide was formed in less than 0.4% yield. Similar results were obtained by gas chromatographic analysis of the crude reaction mixture before silver treatment; however, decomposition products of the allylic bromide interfered with analysis. Since the yield of lithium reagents in the LiDBB reaction was determined to be at least 90%, the syn radical concentration

---

(19) Boche, G.; Schneider, D. R.; Wintermayr, H. *J. Am. Chem. Soc.* **1980**, *102*, 5697.

(20) Jefford, C. W.; Medary, R. T. *Tetrahedron* **1967**, *23*, 4123.

was at least 200 times that of the anti. It is interesting



to note that the syn lithium reagent reacts with ethylene dibromide with at least 99.5% retention. This is in the face of not inconsiderable compressional strain.

Reactions with Noncyclopropyl Secondary Halides

If the product stereochemistry resulting from the reaction of a cyclopropyl radical with lithium 4,4′-di-*tert*-butylbiphenyl represents the radical configuration on a one-to-one basis, then what meaning can be ascribed to the product configuration resulting from a noncyclopropyl cyclic secondary radical? Such radicals run the gamut from essentially planar to fairly pyramidal.[21] The electron transfer would again be expected to be very rapid. In addition to the favorable feature that only one charged species is involved in the encounter complex, the model reaction of the diffusion-controlled rate of sodium-naphthalene (as a loose ion pair) with a primary radical suggests that in reactions of this type, bond distortions and solvent reorganization are not important in proceeding to the transition state.[22] In addition, even with an electron transfer to a secondary rather than a primary radical, transfer of the electron is expected to be exergonic.

Stereochemical constraints under normal circumstances are not anticipated for reactions of LiDBB and lithium–naphthalene with radicals in view of the fact that electron transfer between naphthalene moieties can take place at a separation of 9 Å with a rate constant of 10^7 s^{-1} for the free ion.[23] This is revealed dramatically in the stereochemistry of the reactions of LiDBB and lithium–naphthalene with the equilibrium of *syn*- and *anti*-3-tricyclo[3.2.1.0^{2,4}]octyl radicals.

If electron transfer to the radical gives the free anion, is it possible that the anion undergoes equilibration before combining with a cation? Molecular orbital calculations, which are, in general, quite good at predicting the inversion barrier for amines,[15,24] predict[25] that the inversion barrier for carbanions should be quite similar to that of amines. The experimental rate of inversion of dimethylamine is 1.6×10^9 s^{-1}.[26] While a rate of inversion of 10^9 may seem rather rapid, it is actually much too slow to affect the stereochemical outcome of the reaction of a radical with LiDBB. The collapse of the hypothetical alkyl anion–lithium cation ion pair is expected to be very much faster than if the anion were, for example, generated unpaired in a 0.1 M solution. Yet even in the latter case, since the rate constant for diffusive encounters between oppositely charged species in THF solution is greater than 10^{11} L M^{-1} s^{-1} at 25 °C,[27] the rate of capture of the anion by a lithium cation would be at least 10 times the rate of inversion of dimethylamine. All of the systems investigated in this work are cyclic, and most have a fair amount of ring strain. This would be expected to greatly increase the barrier to inversion.[15] Thus it can be concluded that anion equilibration is probably not a factor in determining the product stereochemistry arising from the reaction of a radical and LiDBB.

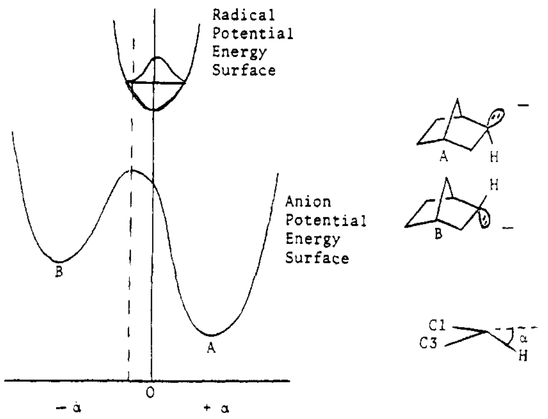


Figure 1.

Our expectation then is that the stereochemistry which is observed in the reaction of a radical with LiDBB can be considered to result from a mapping of the radical probability distribution upon the potential energy curve of the corresponding anion. For purposes of discussion, the 2-norbornyl radical and anion will be used. It will be assumed that the exo anion (A, Figure 1) is more stable than the endo anion (B). An assumed potential energy surface for these anions as a function of the out-of-plane angle, α, is sketched along with the surface for a hypothetical, strictly planar radical. The solid vertical line represents planarity ($\alpha = 0$), while the dashed line represents the division between A and B. If it is assumed that a radical on the B side of the dashed line picks up an electron, it will form anion B and vice versa. Then it can be seen that even in the case of strict planarity of the radical, the more stable anion will be formed in greater abundance than the less stable anion. In fact, the more constrained the radical is, the larger the A/B ratio that results. In reality, it would be expected that the same forces which cause A to be more stable than B would also operate on the radical, but to a lesser degree. This would tend to move the potential energy curve for the radical in the direction of A, and thus give rise to an even greater preponderance of A. If the radical were pyramidal rather than planar, the probability distribution of radicals would correspond to an equilibrium between radical configurations. If the radical were highly pyramidal with the α probability distribution of each configuration not approaching the top of the inversion barrier between A and B, then the product distribution would mirror the radical distribution and be unaffected by the relative stabilities of A and B. It is likely, however, that the relative stabilities of the two radical forms will mimic the relative stabilities of the anions.

Our working hypothesis then is that the organolithium products which result from the reaction of LiDBB with planar radicals give direction and perhaps magnitude information on the relative stabilities of the anions. On the other hand, with significantly pyramidal radicals, information on the direction and magnitude of the radical equilibrium is obtained. Intermediate radical geometries will of course give intermediate results.

Reactions with Secondary Cyclic Halides

7-Norbornenyl System (10). The 7-norbornenyl radical has been a focus of attention in order that a com-

---

[21] Fischer, H. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; p 435.

[22] Eberson, L. In "Advances in Physical Organic Chemistry"; Gold, V., Bethell, D., Ed.; Academic Press: 1982; Vol. 18, p 79.

[23] Shimida, K.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 3313.

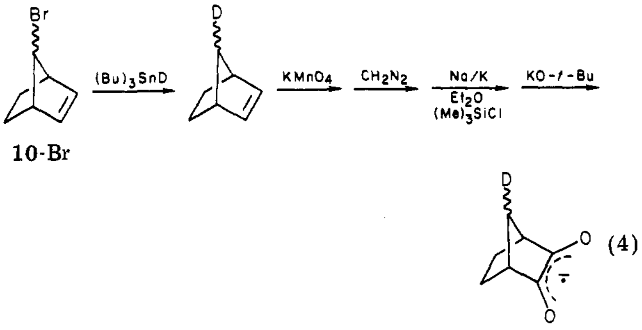
[24] Skaarup, S.; Griffin, L. L.; Boggs, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 3140.

[25] Rauk, A.; Andose, J. D.; Frick, W. G.; Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1971**, *93*, 6507.

[26] Harmony, M. D. *Chem. Phys. Lett.* **1971**, *10*, 337.

[27] Hague, D. N. "Fast Reactions"; Wiley-Interscience: New York, 1971.

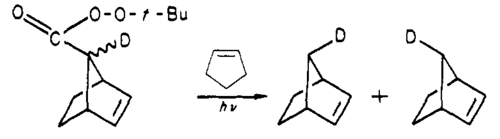
parison might be made with the 7-norbornenyl cation. Warkentin and Sanford[28] originally reported that the reduction of *syn*- or *anti*-7-bromonorbornene (**10**-Br) with tributyltin deuteride gave only anti deuterium incorporation. Their analysis, however, was based upon very noisy NMR spectra of the hydrocarbon. The *syn*- and *anti*-C7 protons were badly overlapped and generally buried in the remainder of the NMR spectrum. A later analysis by Cristol and Noreen[29] provided an estimate that both anti and syn deuterium compounds were present in a ratio of 70:30. Simultaneously, Russell and Holland[30] reported that conversion of the 7-bromonorbornene product in a series of reactions to the semidione (eq 4) followed by ESR analysis indicated an anti/syn ratio of 4.9 ± 0.1.



10-Br

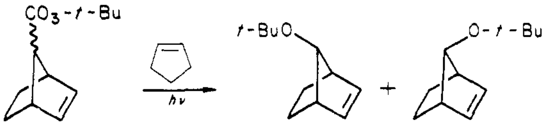
(4)

Kochi, Bakuzis, and Krusic have performed chemical and ESR studies on the 7-norbornenyl radical.[31] Photolysis of the syn or anti deuterated peresters (eq 5 and 6) gave the same mixture of deuterated norbornenes. Photolysis of the nondeuterated peresters gave the same mixture of ethers regardless of the stereochemistry of the starting peresters. The ESR results indicate that the radical is pyramidal, with either a single or double minimum vibrational potential. A double minimum potential function with a deeper well for the anti radical and a low barrier to inversion was considered an attractive rationalization.



(5)

1.9–2.6:1

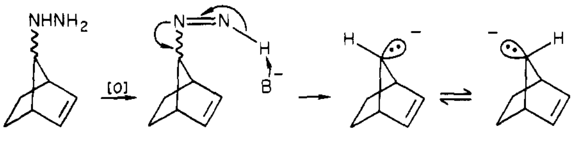


(6)

2.7:1

It is seen that all of the reactions tend to favor the anti position. However, only the last reaction can be regarded as anything approaching the true configurational preference for the radical. While the last process involves radical–radical recombination with approximately zero activation energy, the others have quite substantial activation energies and have been shown in the case of other much more pyramidal systems to involve steric effects.[32-36]

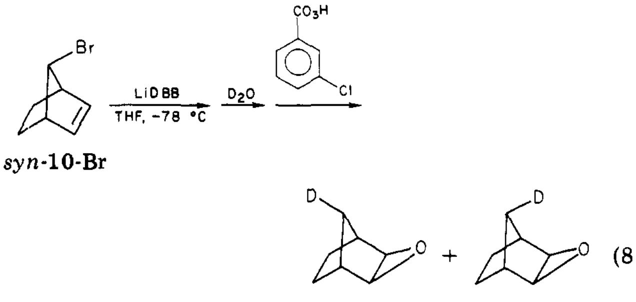
Stille and Sannes[37] have determined that the 7-norbornenyl anion prefers the anti configuration by a factor of 94:6 at 60 °C (eq 7). The anion was produced by basic oxidation of the corresponding hydrazine derivatives (syn and anti) in both deuterium oxide and in *tert*-butyl alcohol-*O*-*d*. The preference for the anti position was explained in terms of an antibonding bishomocyclopropenyl interaction with the double bond in the syn form. The radical might be expected to display characteristics intermediate between that of the carbanion and the corresponding cation.



(7)

6:94

It was of great interest, then, to apply the LiDBB reaction to this very well-studied system. Reaction of *syn*-**10**-Br with LiDBB in THF at −78 °C, followed by deuteriolysis, led to **10**-D. To determine the anti to syn ratio, the norbornene was treated with *m*-choroperbenzoic acid, and the resulting epoxide was analyzed by NMR with the aid of the shift reagent Pr(fod)$_3$. By use of this technique, the *syn*- and *anti*-C7 protons could be separated completely from each other and from all other signals. The results indicate that the anti/syn deuterium ratio was 3.8 ± 0.2:1.



syn-**10**-Br

(8)

3.8:1

Although cyclopropyllithium reagents are well-known to hold their configuration, nothing was known about simple secondary lithium reagents in THF. Since the lithium reagents had to hold their configuration for only 30 s before deuterolysis was performed and since the temperature was quite low (−78 °C), it seems reasonable to assume the deuteration ratio observed is the same as the stereochemistry of the first-formed lithium reagents. To prove that the lithium reagents are capable of holding their configurations, *syn*-**10**-Li was prepared by metal–halogen exchange with *tert*-butyllithium in THF at −50 °C. After only 4 min, almost all of the bromide had reacted, and after 30 min at −50 °C, the reaction was quenched with deuterium oxide. The norbornene was isolated and analyzed as above. Deuterium incorporation was 90%, with a syn/anti ratio of at least 20:1 (eq 9), confirming that the reagents are stable at −78 °C and probably at −50 °C.

It can be readily seen that the lithium reagent ratio obtained in the LiDBB reaction was not due to equilibration of the free anions. If the anti to syn ratio for the

---

(28) Warkentin, J.; Sanford, E. *J. Am. Chem. Soc.* **1968**, *90*, 1667.

(29) Cristol, S. J.; Noreen, A. L. *J. Am. Chem. Soc.* **1969**, *91*, 3870.

(30) Russell, G. A.; Holland, G. W. *J. Am. Chem. Soc.* **1969**, *91*, 3968.

(31) Kochi, J. K.; Bakuzis, P.; Krusic, P. J. *J. Am. Chem. Soc.* **1973**, *95*, 1516.

(32) Singer, L. A.; Kong, N. P. *J. Am. Chem. Soc.* **1966**, *88*, 5213.

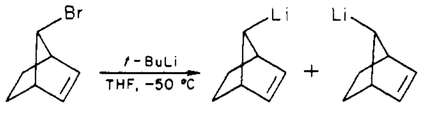
(33) Singer, L. A.; Chen, J. *Tetrahedron Lett.* **1971**, 939.

(34) Altman, L. J.; Baldwin, R. C. *Tetrahedron Lett.* **1971**, 2531.

(35) Ishahara, T.; Hayashi, K.; Ando, T.; Yamanaka, H. *J. Org. Chem.* **1975**, *40*, 3264.

(36) McKinney, M. A.; Anderson, S. W.; Keyes, M.; Schmidt, R. *Tetrahedron Lett.* **1982**, *23*, 3443.

(37) Stille, J. K.; Sannes, K. N. *J. Am. Chem. Soc.* **1972**, *94*, 8489.

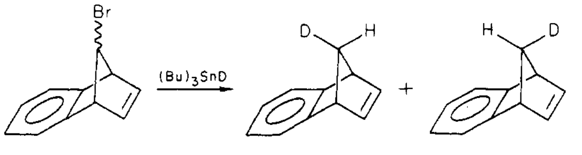


(9)

20:1

free anion equilibrium as determined by Stille is 15 at 60 °C, then it should be on the order of 100 at −78 °C. Thus, it can be concluded that if the 7-norbornenyl radical is significantly pyramidal, then the ratio of anti to syn radicals is 3.8 at −78 °C. At the temperature of Kochi's perester decomposition (32 °C), the anti/syn ratio would be 2.4. This is remarkably similar to the 2.7 ratio obtained for the *tert*-butyl ether products discussed above. The 3.8 anti/syn ratio at −78 °C is also quite close to the 3.5 ratio of *syn*- and *anti*-7-norbornenecarboxaldehyde which has recently been reported for *N*,*N*-dimethylformamide quenching (−78 °C) of 7-lithionorbornene formed from *syn*-**10**-Br and LiDBB according to our procedure.[38]

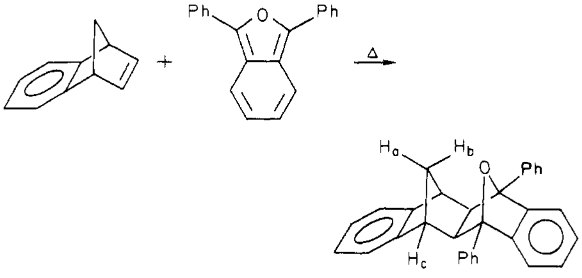
7-Benzonorbornadienyl System (11). Considerable interest has been expressed in radicals and organometallics of this system. Cristol and Noreen[29] reported that the reduction of either *syn*- or *anti*-**11**-Br with tributyltin deuteride gave the same ratio of syn to anti deuterium incorporation of 1.33 (eq 10). Due to severe overlap of NMR signals from the hydrocarbon, analysis was performed by conversion to the Diels–Alder adduct as shown in eq 11. Although H_a is in the clear, H_b is partially overlapped with H_c. This method of analysis was also used by Buske and Ford[39] in their work on the Grignard reaction of **11**-Br and **11**-Cl. The reaction of *syn*- and *anti*-**11**-Cl with sodium–naphthalene and magnesium chloride followed by deuterolysis gave predominantly anti deuteration. However, the ratio of syn to anti was dependent upon the configuration of the starting halide. This is evidence that the anion trapping mechanism of Bank and Bank[40] is not operating in this system. Thus, it is not clear what meaning can be ascribed to the syn to anti ratios which were obtained. The lone-pair orientation of 7-azabenzonorbornadiene in nickel bis(acetylacetonate) complex has been described by two groups. An approximately equal mixture of syn and anti with perhaps a slight excess of the anti form was proposed by Morishima et al.,[41] while Underwood and Friedman conclude that the electron pair is syn to the benzene ring.[42] Even after a reconciliation of the interpretations, the use of shift reagents would still cloud the issue since they are likely to exhibit a discrimination due to steric differences.



(10)

11-Br

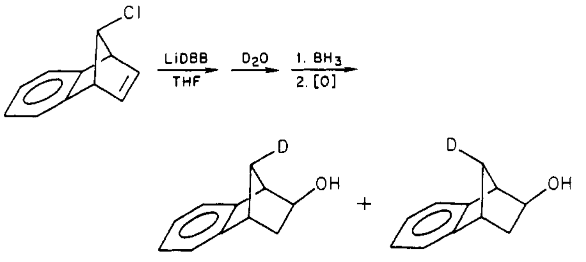
1.33:1



(11)

The ESR spectrum of the 7-benzonorbornadienyl radical at −116 °C has been reported.[43] The α-proton coupling constant (8.3 G) indicated that this radical is somewhat more pyramidal than 7-norbornenyl [$a(H_7)$ = 10.9 G]. The radical was assigned to the anti configuration on the basis of coupling constants alone and with no mention of how much of the syn radical could be in rapid equilibrium with the anti.

The reaction of *anti*-**11**-Cl with LiDBB in THF was carried out at −78 °C, followed 30 s later by deuterolysis. The hydrocarbon was hydroborated and the alcohol analyzed by NMR with the aid of $Pr(fod)_3$. This procedure results in completely unambiguous integrations for both the syn and the anti protons and indicates 99 ± 3% deuterium incorporation with an anti/syn ratio of 1.33 ± 0.02 (eq 12). The deuteration ratio is curiously the same as reported by Cristol and Noreen, but in the opposite direction. If the 7-benzonorbornadienyl radical can be considered significantly pyramidal, then the ratio of anti to syn radical configurations at the temperature of the ESR study discussed above is probably no greater than about 1.5.



(12)

1.33:1

2-Norbornyl System (12). While the α-proton ESR coupling constants for the two previous systems clearly indicate pyramidal geometries, the 2-norbornyl radical would appear to be only slightly pyramidal if at all on the basis of an α hfsc of approximately 21 G. The unequal β $a(H_{3\text{-exo}})$ and $a(H_{3\text{-endo}})$ values support, however, a pyramidal geometry.[44]

The 2-norbornyl radical exhibits a propensity for exo attack. This has been reviewed from the standpoint of stereochemical control of attack upon a planar radical.[45] For example, either the *exo*- or *endo-tert*-butyl peresters gave an exo to endo ratio of *tert*-butyl ethers of 1.65. Either *exo*- or *endo*-2-chloronorbornane in reaction with tributyltin deuteride gave a ratio of exo to endo deuteration of 5.3.[46]

The 2-norbornyl anion has been studied by Stille, Feld, and Freeburger[47] by the same technique described for the 7-norbornenyl anion. At 67 °C, the exo to endo equilibrium value for the anion is at least 30, although the analysis was not as straightforward as in the previous case.

The treatment of *exo*-2-chloronorbornane with LiDBB was performed as usual in THF at −78 °C and followed by deuterolysis. Analysis by IR indicated mostly exo

---

[38] Stapersma, J.; Klumpp, G. W. *Tetrahedron* **1981**, *37*, 187.

[39] Buske, G. R.; Ford, W. T. *J. Org. Chem.* **1976**, *41*, 1988.

[40] Bank, S.; Bank, J. F. *Tetrahedron Lett.* **1969**, 4533.

[41] Yoshikawa, K.; Bekki, K.; Karatsa, M.; Toyada, K.; Kamio, T.; Morishima, I. *J. Am. Chem. Soc.* **1976**, *98*, 3272.

[42] Underwood, G. R.; Friedman, H. S. *J. Am. Chem. Soc.* **1977**, *99*, 27.

[43] Kawamura, T.; Sugiyama, Y.; Matsunaga, M.; Yonezawa, T. *J. Am. Chem. Soc.* **1975**, *97*, 1627.

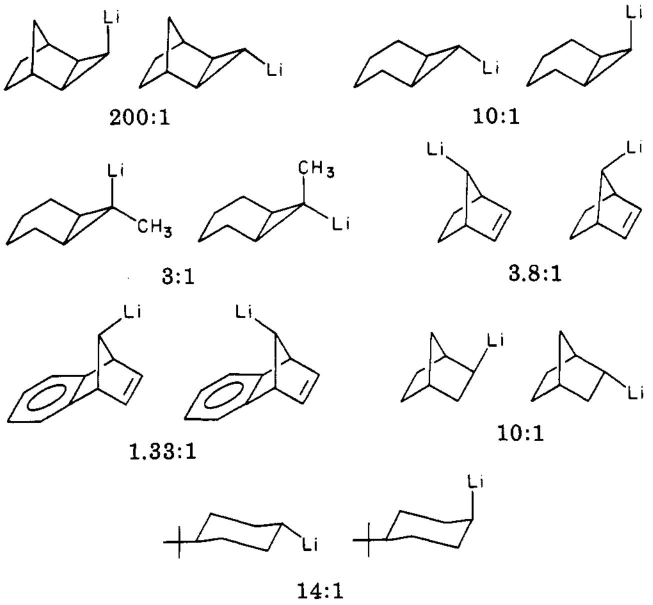
[44] Kawamura, T.; Koyama, T.; Yonezawa, T. *J. Am. Chem. Soc.* **1973**, *95*, 3220; Kawamura, T.; Koyama, T.; Yonezawa, T. *Ibid.* **1970**, *92*, 7222.

[45] Bartlett, P. D.; Fickes, G. N.; Haupt, F. C.; Helgeson, R. *Acc. Chem. Res.* **1970**, *3*, 177.

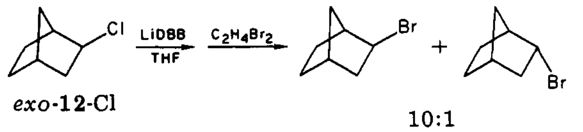
[46] Whitesides, G. M.; Filippo, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 6611.

[47] Stille, J. K.; Feld, W. A.; Freeburger, M. E. *J. Am. Chem. Soc.* **1972**, *94*, 8485.

Chart II. Lithium Reagent Configurations from the Reaction of Radicals with LiDBB in THF at −78 °C

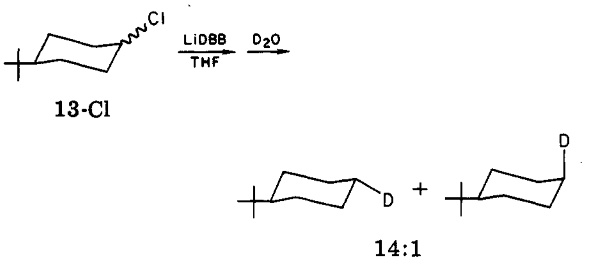


deuteration but was difficult to quantitate. Repetition of the reaction, but with a quench of ethylene dibromide, followed by NMR analysis of the GC-collected bromide peak indicated both *exo*- and *endo*-2-bromonobornanes to be present in a ratio of 10:1 (eq 13).



exo-**12**-Cl (13)

4-*tert*-Butylcyclohexyl System (13). The cyclohexyl radical is generally regarded as being essentially planar, with an α-proton ESR coupling constant of 21.3 G.[48] Treatment of 4-chloro-*tert*-butylcyclohexane with LiDBB in THF at −78 °C followed by deuterolysis gave a mixture of *cis*- and *trans*-**13**-D. IR analysis in the C–D stretching region (see Experimental Section) indicated an equatorial to axial ratio of 14:1 (eq 14). This is in agreement with the conformation of piperidine, which has the lone pair in the equatorial position as determined by shift reagent studies.[49]



13-Cl (14)

A summary of the lithium reagent configurations obtained for the systems in this section and the preceding one is shown in Chart II.

Experimental Section

General Laboratory Procedures and Conditions. All temperatures are uncorrected. NMR spectra were obtained on a Varian HA-100 spectrometer (100 MHz). IR spectra were obtained on a Perkin-Elmer 621 infrared spectrophotometer. Mass spectra were obtained by using an Atlas CH7 mass spectrometer. GC analyses were carried out with a Varian Aerograph A90-P2. Unless otherwise noted, the detector and injector temperatures were set at 230 °C. The flow rate for $^1/_4$ in. columns was generally set at 60 mL/min, with ca. 20 mL/min for $^1/_8$ in. columns. The columns were as follows: column A, 10 ft × $^1/_4$ in., 10% Ucon (water soluble) with 1% KOH on 60–40 Chromosorb W; Column B, 20 ft × $^1/_8$ in. 8% Apiezon N on 80–100 Chromosorb WAS; Column C, 15 ft × $^1/_4$ in., 5% OV-17 on 60–80 Chromosorb G. Ether solvents were distilled from sodium benzophenone dianion and stored over 4A molecular sieves under nitrogen. Errors are standard deviations on multiple integrations (GC or NMR).

General Conditions for the Preparation of Radical Anion Solutions. A 100-mL, three-necked, 14/20 Morton flask containing a 2.5-cm glass-covered magnetic stir bar was simultaneously dried and filled with argon by passing a steady stream of the gas in through the right-hand neck of the flask with alternately one and then the other of the two stoppers floating in the exiting argon stream, while heating the flask with a high-temperature heat gun. After the flask had cooled to about 35 °C, the weighed amount of *p,p*′-di-*tert*-butylbiphenyl was added through a briskly exiting stream of argon via a 14/20 funnel. The required amount of solvent was then added by carefully pouring from the storage container while passing a rapid stream of argon through the flask. The space above the liquid in the storage container was blown out with nitrogen as soon as possible (within 10 s) after the addition. The required amount of lithium metal was weighed out on an analytical balance to within 1–2 mg of the target weight. An oversize piece was first weighed and then trimmed to the proper weight with a knife, cleaning off any oxide crust in the process. The lithium was then placed in the center neck of the flask, and, with a rapid flow of argon, portions of the metal were flattened with curved surgical scissors, so as to maximize the clean surface area, and cut into the solution. A 35-mg piece of lithium typically was cut into, at most, three pieces. This procedure was found to result in more rapid formation of the radical anion than cutting many small pieces of lithium into the solution.

The color of the radical anion pervaded the solution within 10–20 s after the first piece was dropped in. The solution was cooled to 0 °C to prevent excessive decomposition during the formation. The solution was stirred rapidly until no unreacted metal could be discerned in the dark solution. This required typically 3–4 h for LiDBB formation in THF.

Standard conditions A: THF (30 mL), *p,p*′-di-*tert*-butylbiphenyl (6 mmol), and lithium (5 mmol) were treated as in the general conditions above. This results in a solution 0.17 M in LiDBB.

Standard conditions B: As in A above but with the addition of 20 μL (1.56 mequiv) of Br_2. This results in a solution 0.11 M in LiDBB and 0.05 M in LiBr.

Stereochemistry of the Reaction of 7-Chloronorcarane (3-Cl) with LiDBB. To a solution of LiDBB made under conditions A and cooled to −78 °C was added (2 × 100 μL) 7-chloronorcarane (syn/anti ratio of 1.5). The solution was allowed to stir for 15 min at which time D_2O (2 mL) was added, and the solution was allowed to warm to 0 °C. The reaction was worked up in the normal way and separation of the product from DBB was accomplished by bulb to bulb distillation at 1 atm and 160 °C. GC collection of the distillate by using column C at 90 °C followed by NMR analysis indicated greater than 100% deuterium incorporation. This is symptomatic of impurities in the sample. If the deuterium incorporation is assumed to be 95% (the lithium reagent yield from the carbonation experiments), the anti/syn ratio is 5:1. A similar run but with 1 g of LiBr added indicated 87% D incorporation and an anti/syn ratio of 5.6.

Preparation of *syn*- and *anti*-7-Lithionorcarane (3-Li) and Reaction with D_2O. A mixture of *syn*- and *anti*-7-bromonorcarane prepared by the method of Martel and Hiriart[50] was subjected to GC separation (180 °C, column C). NMR of the *syn*-bromide displayed a triplet at δ 3.24 (J = 8.0 Hz) while the corresponding triplet for the *anti*-bromide is at δ 2.53 (J = 3.4 Hz). Each bromide (ca. 50 μL) was treated separately with 1 mL

---

[48] Kochi, J. K., Ed. "Free Radicals"; Wiley: New York, 1973; Vol. 2, p 479.

[49] Morishima, I.; Yoshikawa, K.; Okada, K. *J. Am. Chem. Soc.* **1976**, *98*, 3787.

[50] Martel, B.; Hiriart, J. M. *Synthesis* **1972**, 201.

of 2.3 M *n*-BuLi (hexane, Ventron) and 5 mL of THF at −15 °C. After 10 min, 1 mL of D_2O was added. Workup and GC collection was followed by NMR analysis (CCl_4): from the syn bromide, δ 0.51 (t, *J* = 8.75 Hz); from the anti bromide, δ −0.02 (*J* = 5.5 Hz). Deuteration is above 95% (only one of the two possible C7 protons was observed in each case). Treatment of a mixture of *anti*- and *syn*-bromides in a ratio of 1.33 ± 0.02 with *n*-BuLi followed by D_2O as above gave 80% D incorporation in a ratio of 1.39 ± 0.15 anti to syn.

Stereochemistry of the Reaction of 7-Lithionorcarane with Ethylene Dibromide. A solution of *syn*-7-lithionorcarane was prepared by adding 25 μL of pure GC-collected *syn*-7-bromonorcarane to a solution of 1 mL of *n*-BuLi (2.5 M, Ventron) and 25 mL of THF at −78 °C, followed by warming to 0 °C for 5 min. An aliquot showed no bromide to be present. The solution was cooled to −78 °C, and an excess of ethylene dibromide (220 μL) was then syringed in. An analysis of an aliquot showed only *syn*-7-bromonorcarane with less than 1% anti isomer. The same procedure was repeated for the *anti*-bromide with the result that only the *anti*-bromide was observed for the sequence.

A mixture of *syn*- and *anti*-bromides with an anti/syn ratio of 1.33 ± 0.02 was subjected to the above procedure. GC analysis on column C at 140 °C with dodecane as an internal standard indicated an overall yield of 92% for the *anti*-bromide and 84% for the syn, with the final anti/syn ratio being 1.45 ± 0.02.

Stereochemistry of the Reaction of *anti*-3-Chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane (*anti*-2-Cl) with LiDBB. To a solution of LiDBB in THF at −78 °C made under conditions B was added the internal standard (dodecane, 22.3 mg) followed by the title chloride (48.6 mg). After 15 min, 220 μL of 1,2-dibromoethane was added in one injection. The mixture was warmed to 0 °C, and an aliquot was treated with excess $AgNO_3$ in H_2O for 5 min, followed by the usual extraction procedure. Other than solvent and internal standard, the GC (column C at 140 °C) showed only a small peak at the retention time of the anti-bromide. On the basis of a 90% yield of the lithium compounds (see Table I), the ratio of syn to anti lithium is at least 200:1. Repetition of the above reaction but with D_2O as the quench, followed by NMR analysis of the deuterated hydrocarbon, gave results identical with the lithium naphthalenide experiment (e.g., 100:1 syn/anti deuteration).

Preparation of *anti*-7-Bromo-7-methylnorcarane (*anti*-9-Br). The title compound was prepared by a modification of the procedure of Kitatani, Hiyama, and Nozaki.[51] To a mixture of 40 mL of THF, 10 mL of TMEDA (Aldrich), and 10 g of 7,7-dibromonorcarane, which was cooled to −78 °C, was added 4 g of CH_3I over a period of 1 min. To this mixture was then added dropwise, 16 mL of 2.5 M *n*-BuLi (hexane, Ventron) over a period of 15 min. After warming to 0 °C, the reaction mixture was worked up as usual and subjected to vacuum distillation through a 38-cm 14/20 Vigreux column. The material boiling between 66.4 and 66.5 °C at 5.2 torr weighed 5 g and was about 99% pure by GC (column C at 160 °C, injection port 170 °C): NMR (CCl_4) δ 1.69 (s, CH_3), complex series of absorptions from 1.1 to 2.0.

Reduction of *anti*-7-Bromo-7-methylnorcarane (*anti*-9-Br) with Sodium in *tert*-Butyl Alcohol. To ca. 1 g of the title bromide dissolved in 5 mL of THF and 2 mL of *t*-BuOH was added 0.2 g of Na slices. The mixture was stirred at room temperature for 3 h, at which point no starting bromide was present. Analysis on column B at 100 °C indicated the presence of two products on a ratio of 3:1, with the material of shorter retention time predominating. GC collection using column C at 100 °C and NMR analysis indicated the larger peak to be *anti*-7-methylnorcarane: NMR (CCl_4) δ 1.73 (4 H, br), 1.19 (4 H, br), 1.01 (3 H, d, *J* = 5.5 Hz, CH_3), 0.52 (2 H, br), 0.33 (1 H, complex). The minor peak is assigned the structure *syn*-7-methynorcarane: NMR (CCl_4) δ 1.83 (2 H, br), 1.26 (6 H, complex), 0.98 (3 H, d, *J* = 5.5 Hz, CH_3), 0.76 (3 H, br); IR (CCl_4) 940, 960, 1080, 1180, 1390, 1455, 1465, 3005 cm^{-1}.

Reaction of *anti*-7-Bromo-7-methylnorcarane (*anti*-9-Br) with LiDBB with Dibromoethane Quench. To a solution of LiDBB in THF at −78 °C made under conditions A was added 400 mg of the title bromide. An aliquot was taken in the usual way, and hydrolysis and GC analysis on column F at 100 °C showed two peaks in a ratio of 2.75, with the *anti*-methyl compound predominating. Treatment of the remainder of the reaction mixture with 450 mg of dibromoethane was followed by GC analysis, which showed two peaks in the bromide region with a ratio of 1.5. GC collection and NMR analysis showed the minor component to be identical with the starting material, while the major component's NMR was compatible with the structure *syn*-7-bromo-7-methylnorcarane: NMR (CCl_4) δ 1.76 (s), complex pattern from 1.9 to 1.0 and a highly split absorption centered at 0.84.

Metal–Halogen Exchange of *anti*-7-Bromo-7-methylnorcarane (*anti*-9-Br). To a mixture of 1 mL of 2.3 M *t*-BuLi in pentane (Ventron) and 10 mL of THF maintained at −78 °C was added 50 μL of nonane followed by 90 μL of the title bromide. After 5 min had elapsed, an aliquot was taken and quenched in water, and the remainder of the reaction mixture was treated with CO_2 as with the radical anion reactions.[1] With the assumption of a unity response factor, *syn*-7-methylnorcarane was formed in 58% yield, while the anti compound was formed in 28% yield. The CO_2 quench revealed that 90% of the syn compound was lithiated vs. less than 4% of the anti. The identity of the hydrocarbon products was indicated by GC retention times on both column B and C at 100 °C. The anti compound was GC collected and its IR spectrum shown to be identical with the corresponding product from the Na/*t*-BuOH reduction.

Metal–Halogen Exchange between *syn*-7-Bromonorbornene (*syn*-10-Br) and *tert*-Butyllithium in THF. A solution of *tert*-butyllithium in THF was prepared by injecting 1 mL of 2.3 M *tert*-butyllithium in pentane (Ventron; **Caution**, very pyrophoric) into 10 mL of THF maintained at 50 ± 5 °C. After 5 min, 80 μL of the title bromide was injected all at once. After 4 min, most of the starting bromide was absent, and after 22 min, none was observed. After 30 min, 1 mL of D_2O was added and the mixture worked up as usual. GC collection from column B at 55 °C gave 29 mg of a low-melting solid whose NMR is consistent with 7-deuterionorbornene contaminated with a material giving rise to a sharp singlet at δ 0.8, probably 2,2,3,3-tetramethylbutane.

The olefin was epoxidized by treatment with 70 mg of *m*-chloroperbenzoic acid (Aldrich, 85%) in 1 mL of CH_2Cl_2 at 10 °C. After being allowed to stand at 20 °C for 15 min, the solution was extracted with 3 M NaOH (5 × 5 mL) and then worked up in the usual manner. GC collection was accomplished by using column A at 110 °C with the detector and injector both at 100 °C. Temperatures above 150 °C were found to cause decomposition of the epoxide. The white crystals (16 mg) were dissolved in CCl_4, and $Pr(fod)_3$ was added until the 2- and 3-position protons were at 140 Hz upfield of Me_4Si. At this point in the addition, the *syn*-C7 proton was 188 Hz, the *anti*-C7 proton was 84 Hz, and the *endo*-5,6-protons were 14 Hz upfield of Me_4Si, with the *exo*-5,6-protons at 47 Hz and the bridgehead protons 55 Hz downfield of Me_4Si. The integrations of the *syn*- and *anti*-7-protons relative to the 2,3-protons indicated a 90% D incorporation with at least a 20:1 syn/anti deuterium ratio.

Stereochemistry of the Reaction of *syn*-7-Bromonorbornene (*syn*-10-Br) with LiDBB. To a solution of LiDBB in the THF made under conditions A and cooled to 78 °C was added the title bromide (2 × 100 μL). After 30 s, 2 mL of D_2O was added, and the mixture was worked up as usual. Separation of the olefin from the DBB was accomplished by bulb to bulb distillation at 150 °C for 45 min. The crude distilled product was epoxidized as in the case of the metal–halogen exchange reaction described immediately above and was analyzed by NMR: 90% D incorporation and an anti/syn ratio of 3.8 ± 0.2.

Reaction of *anti*-7-Chlorobenzonorbornadiene (*anti*-11-Cl) with LiDBB. To a LiDBB solution made up according to conditions A and cooled to −78 °C was added dropwise over a period of 45 s a solution of 0.30 g (1.7 mmol) of the title chloride dissolved in 1.0 mL of THF. Within 30 s, 2 mL of D_2O was added. The product was worked up in the usual way, and the deuterated hydrocarbon was separated from DBB by bulb to bulb distillation with an Aldrich Kugelrohr apparatus at 140 °C and 10 torr for ca. 20 min. A portion of the olefin was hydroborated and the alcohol GC collected from column C at 200 °C. $Pr(fod)_3$ was added to the alcohol in CCl_4 until the *endo*-2-proton (α to OH) was 558

---

(51) Kitatani, K.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1975**, *97*, 949.

Hz upfield of Me_4Si. At this point, the 1-bridgehead proton was 334 Hz, the *endo*-3-proton is 320 Hz, the *exo*-3-proton is 610 Hz, the *syn*-7-proton is 472 Hz, and the *anti*-7-proton is 208 Hz upfield of Me_4Si. Integration of the *syn*- and *anti*-7-proton signals relative to the other four protons indicates 99 ± 3% D incorporation and an anti/syn deuterium ratio of 1.33 ± 0.02 (syn or anti is relative to the benzo ring).

Stereochemistry of the Reaction of *exo*-2-Chloronorbornane with LiDBB. To a solution of LiDBB made under conditions A and cooled to −78 °C was added *exo*-2-chloronorbornane (2 × 100 μL) prepared from norbornene and HCl by the method of Schmerling.[52] After 30 s, 1 mL of D_2O was added, and the clear solution was warmed to 0 °C and worked up in the usual manner followed by GC collection from column C at 70 °C. IR analysis at 858 cm^{-1} for the exo and 836 cm^{-1} for the endo isomer as recommended by Nickon and Hammons[53] indicates a 5:1 exo to endo ratio, assuming equal molar extinction coefficients. The analysis is less than fully satisfactory, however, due to severe overlap of absorptions in this region.

In like fashion, reaction of the title chloride (320 mg, 5% excess) with LiDBB solution (from which 2 mL had been removed for other purposes) was followed by quenching within 30 s with excess ethylene dibromide. The solution was warmed to 0 °C and worked up in the usual way. GC analysis showed only one peak in the bromide region. GC collection and NMR analysis of this peak indicates it to be a mixture of 91% *exo*- and 9% *endo*-bromides. The ratio was determined by NMR integrations of the proton α to bromine which for the *exo*-bromide falls at δ 3.9, cleanly separated from the α proton of the *endo*-bromide which falls at δ 4.2.[54]

Stereochemistry of the Reaction of 4-Chloro-*tert*-butylcyclohexane with LiDBB. To a THF solution of LiDBB at −78 °C made under conditions B was added ca. 220 mg of the title chloride prepared by the method of Glaze et al.[55] (cis/trans ratio of 4). After 5 min, D_2O (2 mL) was added, followed by the usual workup. The product was separated from the DBB by bulb to bulb distillation with an Aldrich Kugelrohr apparatus at 210 °C for 10 min. GC collection (column C at 120 °C) was followed by ir analysis in the C-D stretching region. The spectrum was calibrated with an indene external standard by using the 2305-, 2173-, and 2050-cm^{-1} bands. The ratio of equatorial to axial deuteration is at least 14:1 on using the frequencies given by Glaze et al. for the axial and equatorial compounds and assuming that the molar extinction coefficients for the two compounds are approximately the same.

Registry No. 1, 61217-61-6; *anti*-**2**-Cl, 6518-27-0; *anti*-**2**-D, 52882-75-4; *syn*-**2**-D, 52882-74-3; *anti*-**3**-Br, 1121-41-1; *syn*-**3**-Br, 1121-40-0; *anti*-**3**-Cl, 18688-21-6; *syn*-**3**-Cl, 18688-22-7; *anti*-**3**-D, 87461-78-7; *syn*-**3**-D, 87461-79-8; *anti*-**9**-Br, 55027-63-9; *syn*-**9**-Br, 13307-66-9; *anti*-**9**-D, 87481-43-4; *syn*-**9**-D, 87481-44-5; *syn*-**10**-Br, 20047-65-8; *anti*-**10**-D, 20664-22-6; *syn*-**10**-D, 37907-29-2; *anti*-**11**-Cl, 10239-89-1; *anti*-**11**-D, 31893-09-1; *syn*-**11**-D, 51348-79-9; *endo*-**12**-Br, 13237-87-1; *exo*-**12**-Br, 2534-77-2; *exo*-**12**-Cl, 765-91-3; *endo*-**12**-D, 22642-75-7; *exo*-**12**-D, 22642-76-8; *cis*-**13**-Cl, 13131-74-3; *trans*-**13**-Cl, 13145-48-7; *cis*-**13**-D, 53042-76-5; *trans*-**13**-D, 17553-36-5; $C_2H_4Br_2$, 106-93-4; BuLi, 109-72-8; 7,7-dibromonorcarane, 2415-79-4; *anti*-7-methylnorcarane, 14135-43-4; *syn*-7-methylnorcarane, 14222-39-0.

---

(52) Schmerling, L. *J. Am. Chem. Soc.* **1946**, *68*, 195.

(53) Nickon, A.; Hammons, J. *J. Am. Chem. Soc.* **1964**, *86*, 3323.

(54) Applequist, D. E.; Chmurny, G. N. *J. Am. Chem. Soc.* **1967**, *89*, 875.

(55) Glaze, W. H.; Selman, C. M.; Ball, A. L., Jr.; Bray, L. E. *J. Org. Chem.* **1969**, *34*, 641.

Chemistry en Route to $\Delta^{2,2'}$-Bithieno[3,4-*d*]-1,3-dithiole (DTTTF) and Its Selenium Analogue

Long-Yong Chiang

Corporate Research Laboratory, Exxon Research and Engineering Company, Linden, New Jersey 07036

Paul Shu, Dennis Holt, and Dwaine Cowan*

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Received March 18, 1983

Thieno[3,4-*d*]-1,3-dithiole-2-thione (**4**) and its selenium analogue (**11**) were prepared by utilizing the insertion reaction of elemental sulfur and selenium into the carbon–lithium bond as a key step. The coupling reaction of selone **6** or carbene **9**, which were efficiently derived from the corresponding thione through a common intermediate, hexafluorophosphate salt **5**, gave DTTTF (**1**). A similar approach to the synthesis of DTTSF (**2**) and its key intermediate selone **13** is also described. The repeated insertion reaction of microcrystalline tellurium with lithiated thiophene followed by the treatment with thiocarbonylbis(imidazole) gave a mixture of tellurium compounds **16** and **17**.

Salts of certain planar π-electron donor and acceptor molecules form crystals consisting of parallel chains of stacked molecular ions. This class of compounds displays a range of electrical conductivity[1,2] from insulators [DBTTF–TCNQ] to anisotropic metals [TTF–TCNQ] and superconductors [$(TMTSF)_2ClO_4$]. Studies of these and related compounds have provided a better understanding of charge and spin density waves, Peierls transitions, Kohn

---

(1) (a) Cowan, D.; Kini, A.; Chiang, L-Y.; Lerstrup, K.; Talham, D.; Poehler, T.; Bloch, A. *Mol. Cryst. Liq. Cryst.* **1982**, *86*, 1741–66. (b) Cowan, D.; Shu, P.; Hu, C.; Krug, W.; Carruthers, T.; Poehler, T.; Bloch, A. "*Chemistry and Physics of One-Dimensional Metals*"; Plenum: New York, 1977; pp 25–46. (c) Bloch, A. N.; Carruthers, T. F.; Poehler, T. O.; Cowan, D. O. *Ibid.* pp 47–85. (d) Jerome, D.; Schulz, H. J. *Adv. Phys.* **1982**, *31*, 299–490.

(2) Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* (*Orsay, Fr.*) **1980**, *41*, 95–98. Ribault, M.; Benedek, G.; Jerome, D.; Backgaard, K. *J. Phys. Lett.* **1980**, *41*, 397. Bechgaard, K.; Corneiro, K.; Olsen, M.; Rasmussen, F.; Jacobsen, C. *Phys. Rev. Lett.* **1981**, *46*, 852. Gubser, D. U.; Fuller, W. W.; Poehler, T. O.; Cowan, D. O., Lee, M.; Potember, R. S.; Chiang, L-Y.; Bloch, A. N. *Phys. Rev. B*, **1981**, *24*, 478.

0022-3263/83/1948-4713$01.50/0