due in part to slightly different geometries. Neither of these spectra bears a close similarity to those of octahedral $Ni(dipy)_3^{2+}$,[17] $Ni(py)_6^{2+}$,[18] and tris(N-methylpyridinaldimino)nickel(II) cation (DMSO-d_6 solution), with a notable difference being that the narrowest signal experiences the largest shift in the $[Ni(PccBF)]^+$ and $[Ni(py_3tach)]^{2+}$ spectra. These and other spectral and magnetic properties of PccBF and various sexadentate and trischelate-octahedral complexes of Co(II) and Ni(II) are currently being analyzed in order to establish structural criteria. Finally, it is noted that the infrared spectra of the crystalline Co(II), Ni(II), and Zn(II) PccBF complexes are essentially identical, whereas that of $[Fe(PccBF)]^+$ exhibits small differences in the 1600–1500- and 1250–1150-cm^{-1} regions. These may be associated with a greater tendency of the coordinated d^6 ion to distort away from TP geometry and, if so, finds analogy with the near-D_3 structure of $Co^{III}[(dmg)_3(BF)_2]^+$ and the near-TP structure of its neutral Co(II) reduction product.[2]

Lions,[19] in his topological analysis of sexadentate ligands, explicitly recognized 36 types including the open trifurcated[5,14,15,16b] (*e.g.*, py_3tach) and macrocyclic unbranched types, the latter of which have been synthesized subsequently.[20] This and other recent work[2] demonstrate how additional sexadentate patterns may be obtained by producing trifurcations at nondonor atoms, and serve to augment significantly the structural varieties of known sexadentates.

Acknowledgment. This research has been supported by Grants No. NIH GM-15471 and NSF GP-7576X. We thank Dr. L. H. Pignolet and J. G. Gordon, II, for experimental assistance.

(17) M. Wicholas and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6946 (1968).
(18) R. E. Cramer and R. S. Drago, *ibid.*, **92**, 66 (1970).
(19) F. Lions, *Rec. Chem. Progr.*, **22**, 69 (1961).
(20) J. D. Curry and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 592 (1964); L. F. Lindoy and D. H. Busch, *ibid.*, **91**, 4690 (1969); D. St. C. Black and I. A. McLean, *Chem. Commun.*, 1004 (1968).

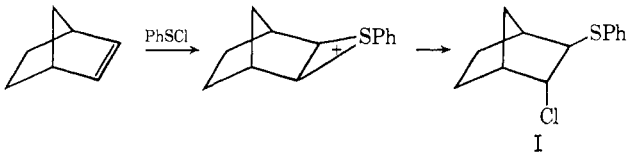
J. E. Parks, B. E. Wagner, R. H. Holm
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received February 25, 1970

Formation of *endo*-2-Phenylthio-*exo*-3-chloro-7,7-dimethylnorbornane from the Addition of Benzenesulfenyl Chloride to 7,7-Dimethylnorbornene. Further Evidence for Dominant Steric Control by 7,7-Dimethyl Substituents on the Direction of Additions to the Norbornene Moiety

Sir:

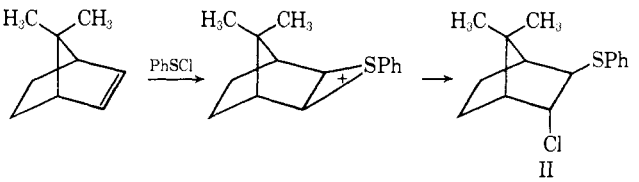
Recently a new interpretation was proposed for the influence of 7,7-dimethyl substituents on the stereochemistry of additions to norbornenes. For additions proceeding through cyclic transition states or intermediates, or the formation of π complexes, these substituents should direct the reaction either to proceed preferentially *endo* or to hinder the reaction so effectively that it fails to occur.[1] Examples of reactions which go preferentially *exo* with norbornene but *endo* with 7,7-dimethylnorbornene are hydroboration, hydrogenation, and epoxidation.[1] Examples of reactions which proceed quite satisfactorily with norbornene but fail with the 7,7-dimethyl derivative are silver ion complexation,[1] addition of phenyl azide,[2] and addition of chlorosulfonyl isocyanate.[3]

One apparent exception exists. The addition of benzenesulfenyl chloride to olefins is considered to proceed *via* an episulfonium ion intermediate.[4] Thus, norbornene yields exclusively *exo*-2-phenylthio-*endo*-3-chloronorbornane (I), presumably through displacement by chloride ion on the *exo*-episulfonium ion.[5]



I

Mueller and Butler also reported that the addition to 7,7-dimethylnorbornene proceeds with the same stereochemistry to give an *exo*-2-phenylthio-*endo*-3-chloro adduct (II) with 85% selectivity based on the pmr spectra of II and its corresponding sulfone III.[6] Obviously the proposed stereochemistry requires that the *exo* cyclic intermediate must be more stable than the corresponding *endo* intermediate in spite of the presence of the sterically demanding 7,7-dimethyl substituents. This contradicts the proposed generalization.



II

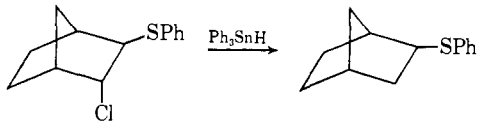
In attempting to rationalize this apparent exception to the proposed generalization, we noted that the pmr chemical shift of the two α-methine protons in II and in III were not in line with the change in chemical shift of the α-methine proton brought about by the introduction of 7,7-dimethyl substituents into norbornane derivatives of established stereochemistry.[7] Therefore, we undertook to reexamine the structure of the benzenesulfenyl chloride–7,7-dimethylnorbornene adduct by an unambiguous chemical method. Such a method was found in the treatment of the adducts with triphenyltin hydride.[8] It successfully removed the chlorine substituent and allowed the stereochemistry of the re-

(1) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).
(2) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **501**, 1 (1933); **515**, 185 (1935).
(3) E. J. Moriconi and W. C. Crawford, *J. Org. Chem.*, **33**, 370 (1968).
(4) W. H. Mueller, *Angew. Chem. Int. Ed. Engl.*, **8**, 482 (1969), and references cited therein.
(5) W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **88**, 2866 (1966). See also S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, *ibid.*, **79**, 6035 (1957).
(6) W. H. Mueller and P. E. Butler, *ibid.*, **90**, 2075 (1968).
(7) Introduction of 7,7-dimethyl substituents causes only a small downfield shift ($\leq$0.1 ppm) of the *endo* proton but a comparatively large downfield shift ($\geq$0.3 ppm) of the *exo* proton. However, the *exo* proton in II (δ 4.08) only shows a small downfield shift as compared with that in I (δ 3.99), whereas the *endo* proton in II (δ 3.73) displays a large downfield shift relative to that in I (δ 3.04). The discrepancy is even worse for the sulfone II, since the *exo* proton in III (δ 3.95[6]) exhibits an upfield shift as compared with that in *exo*-2-benzenesulfonyl-*endo*-3-chloronorbornane (δ 4.45).
(8) H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963). We are indebted to Dr. Charles A. Brown for suggesting this solution.

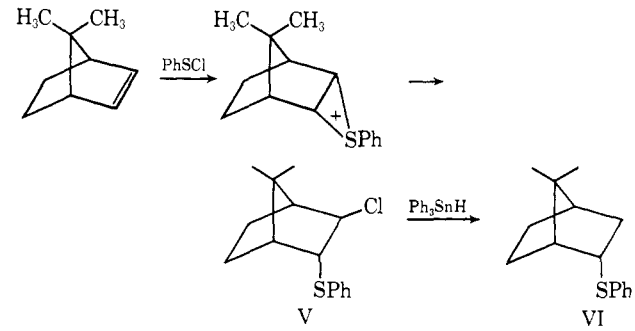
maining phenylthio group to be established by glpc comparison with the known phenyl sulfides.

Benzenesulfenyl chloride was slowly added to a methylene chloride solution of 7,7-dimethylnorbornene containing a small amount of suspended calcium carbonate at −20°.[6] The crude adduct (IV), a semisolid, was obtained quantitatively. The pmr spectrum[9] of IV revealed that it contained about 80% of one major product, V. Recrystallization of IV with petroleum ether (bp 35–37°) yielded 60% of pure V, mp 42.5–43° (lit.[6] mp 35–38°). *Anal.* Calcd for $C_{15}H_{19}SCl$: C, 67.52; H, 7.18; S, 12.02; Cl, 13.28. Found: C, 67.70; H, 7.10; S, 12.22; Cl, 13.48. The pertinent pmr data of V are identical with those of II as reported:[6] a doublet (J = 4.8 Hz) at δ 3.73 (1 H) and a doublet of an apparent triplet (J = 4.8, 4.3, 1.4 Hz) at δ 4.08 (1 H). The observed splitting patterns and coupling constants indicate a *trans* relationship with an *exo* proton at δ 4.08 and an *endo* proton at δ 3.73. The chemical shifts of the *endo* α-methine proton in V (δ 3.73), its corresponding sulfone (δ 4.37[6]), and 7,7-dimethyl-*exo*-norbornyl chloride (δ 3.90) suggested an *exo*-chloro-*endo*-phenylthio orientation.[10]

To achieve the desired hydrodechlorination I was heated for 1 hr at 80° with triphenyltin hydride in the presence of a catalytic amount of azobisisobutyronitrile.[8] A 62% yield of *exo*-norbornyl phenyl sulfide was realized. Under the same conditions a complete



hydrodechlorination of V was observed. The product showed identical glpc retention time with 7,7-dimethyl-*endo*-norbornyl phenyl sulfide (VI), a minor product from the free-radical addition of thiophenol to 7,7-dimethylnorbornene.[1,11] The *endo*-phenyl sulfide VI was isolated using preparative glpc in 60% yield. *Anal.* Calcd for $C_{15}H_{20}S$: C, 77.53; H, 8.67; S, 13.80. Found: C, 77.34; H, 8.60; S, 13.69. The pmr spectrum of VI displays a multiplet at δ 3.85 (1 H) characteristic for an *exo* α-methine proton. The small difference in the chemical shift of the two methyl singlets (δ 1.05 and 1.09) also confirms the *endo* orientation of the phenylthio group.[12] No isomerization of VI to its *exo* isomer or *vice versa* has been detected under the hydrodechlorination conditions. Consequently, the major product obtained from the addition of benzenesulfenyl chloride to 7,7-dimethylnorbornene is in fact the *endo*-2-phenylthio-*exo*-3-chloro adduct V,



and not the alternative isomer II as proposed.[6] The selectivity is at least 80%, since the pmr spectrum indicates the presence of 80% of V in IV, and the hydrodechlorination of IV with triphenyltin hydride reveals 80% of VI (glpc).

The present result therefore removes a major difficulty with the proposal that 7,7-dimethyl substituents exert dominant steric control on addition reactions proceeding through cyclic transition states or intermediates, or the formation of π complexes. Accordingly, this proposal appears capable of providing a tool for exploring and interpreting the mechanisms of additions to norbornenes. For example, oxymercuration of norbornene,[15] 7,7-dimethylnorbornene,[1] and 1,4,7,7-tetramethylnorbornene[16] all give cleanly *exo-cis* adducts. Therefore, a cyclic transition state or intermediate,[16–18] *e.g.*, mercurinium ion, is probably not involved in this addition process.

We continue to test the proposed generalization in an effort to establish its consistency and reliability.

(9) All the pmr spectra were measured as deuteriochloroform solution on a Varian A-60A spectrometer, with tetramethylsilane as internal references.

(10) In norbornyl derivatives the effect of the phenylthio group on the *cis*-vicinal proton is shielding, whereas the effect of the benzenesulfonyl group is deshielding. This can be illustrated by the observed chemical shift of the *exo*-α-methine proton in I (δ 3.99), the corresponding sulfone (δ 4.45), and *endo*-norbornyl chloride (δ 4.18).

(11) Glpc analysis was performed with a 150 ft × 0.01 in. Apiezon L column on a Perkin-Elmer Model 226 gas chromatograph.

(12) For a pair of epimeric 7,7-dimethylnorbornyl derivatives the difference between the two methyl singlets is always larger in the *exo*-substituted epimer than in the *endo* one. For instance, it is 0.18 ppm in 7,7-dimethyl-*exo*-norbornyl tosylate and about zero in the *endo* epimer.[13] In 7,7-dimethyl-*exo*-norbornyl phenyl sulfide the difference is 0.28 ppm.[14]

(13) K.-T. Liu, Ph.D. Thesis, Purdue University, 1968.

(14) J. H. Kawakami, Ph.D. Thesis, Purdue University, 1968.

(15) T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, **No. 19**, 14 (1959); *J. Amer. Chem. Soc.*, **85**, 2746 (1963).

(16) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, 33, 2614 (1968).

(17) A. Factor and T. G. Traylor, *ibid.*, 33, 2607 (1968).

(18) W. Kitching, *Organometal. Chem. Rev.*, 3, 61 (1968), and relevant references cited therein.

(19) Postdoctoral Research Associate on a grant (GP 6492 X) supported by the National Science Foundation.

Herbert C. Brown, Kwang-Ting Liu[19]
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907
Received February 17, 1970

Oxygen-Induced Reactions of Organoboranes with Acetylacetylene. A Convenient New Synthesis of α,β-Unsaturated Ketones *via* Hydroboration

Sir:

Trialkylboranes, readily available *via* hydroboration, undergo facile 1,4 addition to many α,β-olefinic carbonyl compounds.[1,2] These additions are "spontaneous" for numerous such carbonyl compounds, including methyl vinyl ketone,[1] acrolein,[2] α-methylacrolein,[3] α-bromoacrolein,[3] and α-methylenecyclanones.[4] However, β-substituted α,β-olefinic carbonyl compounds require radical initiators to achieve a reaction.[5] Thus trialkylboranes react readily with

(1) A. Suzuki, A. Arase, H. Matsumoto, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 5708 (1967).

(2) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967).

(3) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4165 (1968).

(4) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4166 (1968).