

excited **1** or **2**. Except where noted, the nucleophiles listed in the table do not react with ground states of **1**, **2**, or riboflavin; more reactive nucleophiles such as  $\text{CN}^-$  and aliphatic amines react with ground states of **1** and **2**. Reaction of excited singlets of **2** and **3** with water or ethanol leads to the formation of isolable adducts;<sup>7</sup> however there is no correlation of  $k_q$  values with quantum efficiencies for adduct formation. Several nucleophiles that give higher  $k_q$  values than water, such as ether, pyridine, and inorganic ions, do not produce adducts with either **2** or **3**. For **1**, roughly the same pattern is observed: concentrations of nucleophile high enough to quench most of the fluorescence lead to adduct formation with very low efficiency for chloride ( $\phi \sim 0.001$ ) and acetate ( $\phi \sim 0.004$ ).

Attack of excited states by nucleophiles is not without precedent; photochemical nucleophilic substitution and addition reactions have been previously reported for aromatic nitro compounds<sup>8,9</sup> and aromatic acetylenes.<sup>10</sup> These reactions have been monitored by product formation as opposed to the current observation of excited state deactivation frequently with no product formation. It is perhaps surprising that excited states with supposed diradical character are attacked so readily by nucleophiles; the attack by nucleophiles on radical cations of aromatic hydrocarbons (generated by anodic oxidation)<sup>11</sup> offers an interesting analogy to the present observations.

We have extended our investigation to uncharged substrates such as riboflavin and pyrimidine bases to determine whether the short singlet lifetimes,<sup>12</sup> reported medium and substituent effects on fluorescence,<sup>13</sup> photoaddition,<sup>14</sup> and photohydration<sup>15,16</sup> for these compounds can be attributed, in part, to interactions with nucleophiles. 1,3-Dimethyluracil (**4**) proved to be a useful model compound for quenching studies. Although hydroxide and bromide react with **4** in the ground state, weaker nucleophiles such as acetate, sulfate, and chloride ions do not quench its fluorescence. Fluorescence of **4** is quenched weakly by water ( $k_q\tau = 0.1 M^{-1}$  in acetonitrile); however, dilute HCl (up to 0.1 *M* in 90% water–10% acetonitrile) strongly quenches fluorescence of **4** while promoting no ground-state reaction. Photohydration evidently originates by photoprotonation of excited singlets of **4**;<sup>17</sup> the quenching correlates with an increase in photohydrate yield with decreasing pH.<sup>16</sup> Whether the reported

quenching of purine base fluorescence by ions<sup>19</sup> is due to nucleophilic attack remains to be determined.

Riboflavin presents an interesting case; its strong fluorescence in aqueous solution is quenched both by nucleophiles (Table I) and by acids ( $k_q\tau$  for acetic acid = 2.1  $M^{-1}$ ) which do not react in the ground state.<sup>20</sup> An explanation for this is offered by calculations which suggest increased polarity in excited states of riboflavin.<sup>21</sup> The sensitivity of excited riboflavin toward nucleophiles is probably related to its ease of photo-reduction.<sup>13</sup>

**Acknowledgment.** We are grateful for support of this work by the U. S. Army Research Office, Durham (Grant DA-ARO-D-31-124-G1097), and the National Science Foundation (through a Science Development Award).

(19) D. C. Ward and E. Reich, *J. Biol. Chem.*, **244**, 1228 (1969).

(20) Although rates of quenching by nucleophiles do not correlate well using the Edwards equation, the rates increase qualitatively with increasing nucleophilicity.

(21) P. S. Song, *J. Phys. Chem.*, **72**, 536 (1968).

(22) National Aeronautics and Space Administration Predoctoral Fellow, 1966–1969.

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### Three-Dimensional Macrocyclic Encapsulation Reactions. I. Synthesis of Six-Coordinate Complexes with Nonoctahedral Stereochemistry

Sir:

The original proposal by Busch<sup>1</sup> that complexes containing completely encapsulated metal ions should be obtainable has been followed by the recent synthesis of two such "clathro-chelates" of cobalt,<sup>2</sup>  $[\text{Co}(\text{dmg})_3(\text{BF}_2)_2]^{10+}$ . We report here a synthetic procedure and supporting characterization data which demonstrate entry to a new class of clathro chelates. The members of this class possess a rigid bicyclic ligand structure which is expected to stabilize trigonal prismatic (TP) or near-TP stereochemistry, and thereby facilitate a systematic study of this stereochemistry. In discrete species TP structures have been proven (by X-ray methods) only for  $[\text{Co}(\text{dmg})_3(\text{BF}_2)_2]$ ,<sup>2</sup> certain metal tris(dithiolenes),<sup>3</sup> one diastereoisomer of  $[\text{Co}(\text{Co}(\text{OCH}_2\text{-C}_2\text{H}_4\text{NH}_2)_3)_2]^{2+}$ ,<sup>4</sup> and 1,3,5-tris(2-pyridinaldimino)cyclohexanezinc(II) cation,<sup>5</sup>  $[\text{Zn}(\text{py}_3\text{tach})]^{2+}$ . The structure of the latter complex and the ring-closure reaction of Boston and Rose<sup>2</sup> have been relevant factors

(1) D. H. Busch, *Rec. Chem. Progr.*, **25**, 107 (1964).

(2) (a) D. R. Boston and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6859 (1968); (b) D. R. Boston and N. J. Rose, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR-96. The nearly trigonal prismatic nature of the Co(II) complex has been established by X-ray diffraction (E. C. Lingafelter, *et al.*, submitted for publication; N. J. Rose, private communication).

(3) H. B. Gray, R. Eisenberg, and E. I. Stiefel, *Advan. Chem. Ser.*, No. **62**, 641 (1967); J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968); G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).

(4) J. A. Bertrand, J. A. Kelley, and E. G. Vassian, *J. Amer. Chem. Soc.*, **91**, 2394 (1969).

(5) (a) W. O. Gillum, J. C. Huffman, W. E. Streib, and R. A. D. Wentworth, *Chem. Commun.*, 843 (1969); (b) R. A. D. Wentworth, W. O. Gillum, and R. F. Childers, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR-194.

(7) M. T. McCall and D. G. Whitten, *J. Amer. Chem. Soc.*, **91**, 5681 (1969); in addition we find that quenching of the fluorescence of *trans*-**2** is concurrent with quenching of *trans* → *cis* photoisomerization. Photoisomerization of *trans*-**2** proceeds from the singlet but not from the triplet.

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(9) R. L. Letsinger and J. H. McCain, *J. Amer. Chem. Soc.*, **91**, 6425 (1969).

(10) T. D. Roberts, L. Ardemagni, and H. Schechter, *ibid.*, **91**, 6185 (1969).

(11) R. N. Adams, *Accounts Chem. Res.*, **2**, 175 (1969).

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(13) For a review on flavins see G. R. Penzer and G. K. Radda, *Quart. Rev. Chem. Soc.*, **21**, 43 (1967).

(14) K. C. Smith, *Photochem. Photobiol.*, **7**, 651 (1968).

(15) H. E. Johns, *ibid.*, **7**, 633 (1968).

(16) J. G. Burr, B. R. Gordon, and E. H. Park, *ibid.*, **8**, 73 (1968); J. G. Burr, *Advan. Photochem.*, **6**, 193 (1968).

(17) This contrasts to photoprotonation of cyclic olefins<sup>18</sup> which has been proposed to proceed *via* reaction of a transoid (ground state) photoproduct.

(18) P. J. Kropp, *J. Amer. Chem. Soc.*, **91**, 5783 (1969).

in our approach to the synthesis of the present group of complexes.

The strategy employed in the preparation of complexes with TP ( $C_{3v}$ ) or near-TP ( $C_3$ ) nonoctahedral structures has two requisites: (a) the presence of planar, conjugated five-membered chelate rings bound to two anchoring atoms or groups centered on the  $C_3$  axis so as to prevent substantial relative motion of any three donor atoms; and (b) the formation, in the last synthetic step, of the macrocyclic cage implied in (a) around the metal ion, thereby encapsulating it. 2,6-Dibromopyridine was converted to its monolithio derivative by reaction with *n*-butyllithium in ether at  $-60^\circ$ . Addition of a small excess of dry DMF to the reaction mixture at  $-80^\circ$  followed by warming to  $-30^\circ$  and acid hydrolysis afforded 6-bromopyridine-2-aldehyde<sup>6</sup> (**1**) as white flakes after recrystallization from ether-pentane (75%, mp  $80-81^\circ$ ). Treatment of **1** with ethylene glycol and *p*-toluenesulfonic acid in refluxing benzene for 100 hr yielded, after distillation, 2-(1,3-dioxolan-2-yl)-6-bromopyridine (**2**) as a colorless oil, bp  $120-122^\circ$  (1 mm), 76%. Transmetalation of **2** in ether solution was carried out at  $-100^\circ$  by treatment with *n*-butyllithium. Stoichiometric addition of phosphorus trichloride to this solution and reaction for 6 hr at  $-100^\circ$  gave tris[2-(1,3-dioxolan-2-yl)-6-pyridyl]phosphine (**3**) as a white solid (40%, mp  $137-138^\circ$ , from ethanol). Anaerobic acid hydrolysis of **3** and treatment with hydroxylamine yielded tris(2-aldoximo-6-pyridyl)phosphine<sup>7</sup> (**4**, P(Hpox)<sub>3</sub>) as colorless needles after recrystallization from DMF-ethanol (90%, mp  $239-241^\circ$ ).

Reaction of **4** with  $M(\text{BF}_4)_2$  ( $M = \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Zn(II)}$ ) in hot ethanol afforded nicely crystalline substances whose analyses suggest the formulation  $[M(\text{P}(\text{Hpox})_3\text{-H})(\text{BF}_4)]^+$ . Encapsulation was accomplished by homogeneous anaerobic reaction ( $\sim 12$  hr,  $25^\circ$ ) of these salts with distilled boron trifluoride etherate, a useful reagent for bridging oxime functions.<sup>2,9</sup> Recrystallization from acetonitrile-alcohol or ether gave the pure<sup>10</sup> clathro chelate (cc) complexes  $[M(\text{PccBF})(\text{BF}_4)]$  ( $M = \text{Fe(II)}$ , dark red;  $\text{Zn(II)}$ , colorless, both diamagnetic;  $\text{Ni(II)}$  red-orange, 3.11 BM;  $\text{Co}$ , red-brown, 4.9 BM) in ca. 50% yield from **4**. Conductivities in acetonitrile [ $\sim 10^{-3} M$ ,  $140-150 \text{ cm}^2/(\text{mol ohm})$ ] are consistent with those of 1:1 salts,<sup>2a,11</sup> and infrared spectra ( $1650-950 \text{ cm}^{-1}$ ) exhibit features compatible with previous empirical assignments<sup>2a,9,12</sup>

(6) Unless otherwise indicated all new compounds gave satisfactory elemental analysis and were further identified by their pmr, infrared, and mass spectra where feasible.

(7) The parent trialdehyde has been obtained from the hydrolysis of **3** as a viscous light yellow oil which has not yet been crystallized. It has been identified by its pmr, infrared, and mass spectra. Reactions of the aldehyde with metal ions have not as yet led to isolable products.

(8) Hpox = 2-aldoximo-6-pyridyl group. These complex cations are best isolated as analytically pure perchlorate salts. The loss of one or more protons upon coordination of two or three pyridinaloxime molecules has been previously observed: D. K. Banerjee and K. K. Tripathi, *Anal. Chem.*, **32**, 1196 (1960); R. A. Krause and D. H. Busch, *J. Amer. Chem. Soc.*, **82**, 4830 (1960); C. H. Liu and C. F. Liu, *ibid.*, **83**, 4169 (1961); G. I. H. Hanania and D. H. Irvine, *J. Chem. Soc.*, 2745 (1962); J. Faucherre and C. Petitfoux, *Bull. Soc. Chim. Fr.*, 347 (1965).

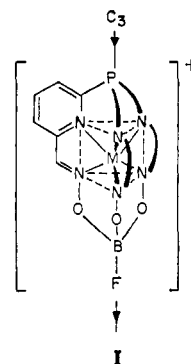
(9) G. N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962).

(10) The analytical purity of the Ni(II) complex is typical of the series. *Anal.* Calcd for  $\text{C}_{12}\text{H}_{13}\text{B}_2\text{F}_5\text{N}_5\text{O}_3\text{PNI}$ : C, 38.34; H, 2.15; N, 14.91; F, 16.85. Found: C, 37.78; H, 2.06; N, 14.47; F, 16.40.

(11) A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 1139 (1968).

(12) R. A. Krause, N. B. Colthup, and D. H. Busch, *J. Phys. Chem.*, **65**, 2216 (1961).

of  $\text{C}\equiv\text{N}$ ,  $\text{N}-\text{O}$ ,  $\text{B}-\text{O}$ ,  $\text{B}-\text{F}$ , and substituted pyridine ring absorptions. The  $^{19}\text{F}$  nmr spectra of all complexes reveal signals due to apical  $\text{BF}$  and  $\text{BF}_4^-$ .<sup>13</sup>  $[\text{M}(\text{PccBF})]^+$  cations are assigned structure I, the minimal trigonal



symmetry of which is demonstrated by the appearance of three pyridine ring proton signals in the strongly isotropically shifted pmr spectra of the paramagnetic  $\text{Co(II)}$  ( $-33$  to  $-130$  ppm) and  $\text{Ni(II)}$  ( $-22$  to  $-67$  ppm) complexes and a single sharp  $\text{HC}\equiv\text{N}$  signal in the spectra of the diamagnetic  $\text{Fe(II)}$  ( $-9.33$  ppm) and  $\text{Zn(II)}$  ( $-8.31$  ppm) complexes ( $\text{DMSO}-d_6$ ,  $\sim 29^\circ$ , TMS reference). The TP or near-TP geometry depicted in I is a consequence of the macrocyclic cage structure, the rigidity and dimensions of which should not allow close approach of the  $\text{M}-\text{N}_6$  coordination unit to an octahedral arrangement.<sup>13a</sup>

With the  $[\text{M}(\text{PccBF})]^+$  complexes in hand, we are engaged in seeking experimental criteria for TP or near-TP coordination in other groups of pyridinaldimine complexes. Those most nearly analogous to the PccBF complexes are members of the  $[\text{M}(\text{py}_3\text{tach})]^{2+}$  series,<sup>5,14,15</sup> which have a potentially more variable stereochemistry because of the presence of only one anchoring (cyclohexyl) group. Magnetic moments of  $[\text{M}(\text{PccBF})]^+$  and  $[\text{M}(\text{py}_3\text{tach})]^{2+}$  complexes parallel each other; the  $\text{Mn(II)}$  and  $\text{Co(II)}$ , but not the  $\text{Fe(II)}$  and  $\text{Ni(II)}$ , members of the latter series are isomorphous with TP  $[\text{Zn}(\text{py}_3\text{tach})]^{2+}$ .<sup>5</sup> Ligand-field spectra of  $[\text{Ni}(\text{py}_3\text{tach})]^{2+}$  and  $[\text{Ni}(\text{PccBF})]^+$  ( $9430 \text{ cm}^{-1}$ ,  $\epsilon$  28;  $11,000 \text{ cm}^{-1}$ ,  $\epsilon$  27) do not resemble those of octahedral tris(diimine)- $\text{Ni(II)}$  complexes<sup>16</sup> and are quite similar to each other except for a red shift of the bands of the latter. The observation of two distinct features of nearly equal intensity supports the contention<sup>15</sup> that the splitting arises from a pronounced or dominant trigonal component of the ligand field. It has been further observed that the chemical shifts of the pyridine ring protons of  $[\text{Ni}(\text{PccBF})]^+$  ( $-23.2$ ,  $-33.9$ ,  $-66.5$  ppm) do not correspond closely to those of  $[\text{Ni}(\text{py}_3\text{tach})]^{2+}$  ( $-15.1$ ,  $-47.0$ ,  $-49.1$  ppm), an effect which may be

(13) For example: diamagnetic  $[\text{Zn}(\text{PccBF})(\text{BF}_4)\text{-BF}]$ ,  $+103$  ppm (quartet,  $J_{\text{BF}} = 11$  Hz);  $^{11}\text{BF}_4^-$ ,  $+86.7$  ppm (quartet,  $J_{\text{BF}} = 0.9$  Hz); paramagnetic  $[\text{Ni}(\text{PccBF})(\text{BF}_4)\text{-BF}]$ ,  $+181$  ppm;  $\text{BF}_4^-$ ,  $+84.7$  ppm. Spectra were obtained in  $\text{DMSO}-d_6$  at  $\sim 29^\circ$  with perfluoromethyltoluene internal reference.

(13a) NOTE ADDED IN PROOF. An X-ray study of  $[\text{Ni}(\text{PccBF})(\text{BF}_4)]$  has confirmed structure I; the twist angle of the two  $\text{N}_3$  triangles from TP coordination is less than  $\sim 2^\circ$  (M. R. Churchill and A. H. Reis, Jr., unpublished results).

(14) F. Lions and K. V. Martin, *J. Amer. Chem. Soc.*, **79**, 1572 (1957).

(15) J. E. Sarneski and F. L. Urbach, *Chem. Commun.*, 1025 (1968).

(16) (a) M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, **2**, 1178 (1963); (b) L. J. Wilson and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6041 (1968).

due in part to slightly different geometries. Neither of these spectra bears a close similarity to those of octahedral  $\text{Ni}(\text{dipy})_6^{2+}$ ,<sup>17</sup>  $\text{Ni}(\text{py})_6^{2+}$ ,<sup>18</sup> 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  $[\text{Ni}(\text{PccBF})]^+$  and  $[\text{Ni}(\text{py}_3\text{tach})]^{2+}$  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  $[\text{Fe}(\text{PccBF})]^+$  exhibits small differences in the 1600–1500- and 1250–1150- $\text{cm}^{-1}$  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  $\text{Co}^{II}[(\text{dmg})_3(\text{BF})_2]^+$  and the near-TP structure of its neutral Co(II) reduction product.<sup>2</sup>

Lions,<sup>19</sup> in his topological analysis of sexadentate ligands, explicitly recognized 36 types including the open trifurcated<sup>9,14,15,16b</sup> (e.g.,  $\text{py}_3\text{tach}$ ) and macrocyclic unbranched types, the latter of which have been synthesized subsequently.<sup>20</sup> This and other recent work<sup>2</sup> 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.

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(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).

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## Formation of

**endo-2-Phenylthio-*exo*-3-chloro-7,7-dimethylnorbornane from the Addition of Benzenesulfonyl 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**

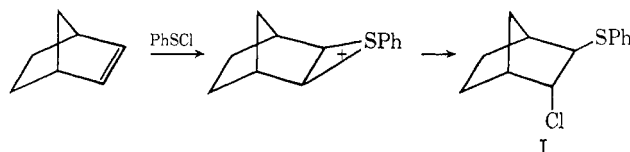
Sir:

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  $\pi$  complexes, these substituents should direct the reaction either to proceed preferentially *endo* or to hinder the reaction so effectively that it fails to occur.<sup>1</sup> Examples of reactions which go preferentially *exo* with norbornene but *endo* with 7,7-dimethylnorbornene are hydroboration, hy-

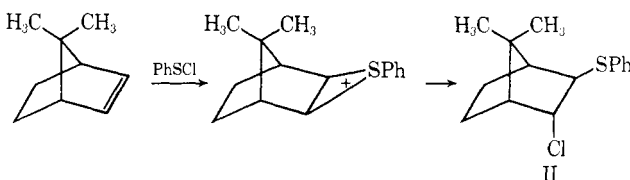
(1) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

drogenation, and epoxidation.<sup>1</sup> Examples of reactions which proceed quite satisfactorily with norbornene but fail with the 7,7-dimethyl derivative are silver ion complexation,<sup>1</sup> addition of phenyl azide,<sup>2</sup> and addition of chlorosulfonyl isocyanate.<sup>3</sup>

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



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.<sup>6</sup> Ob-



viously 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.

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

(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 ( $\delta$  4.08) only shows a small downfield shift as compared with that in I ( $\delta$  3.99), whereas the *endo* proton in II ( $\delta$  3.73) displays a large downfield shift relative to that in I ( $\delta$  3.04). The discrepancy is even worse for the sulfone II, since the *exo* proton in III ( $\delta$  3.95) exhibits an upfield shift as compared with that in *exo*-2-benzenesulfonyl-*endo*-3-chloronorbornane ( $\delta$  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.