clathrates with a single guest,[10] but this is the first example of a TOT analogue displaying the same versatility in clathrate formation as TOT. The space groups, cell dimensions, and host:guest ratios for the TSBS clathrates and the conformation of the host molecule (see below and Figure 1) are the same as those for the corresponding TOT clathrates.

The crystal structure of the TSBS/(*S*)-(+)-2-butanol clathrate[11] (Figure 1) shows that all of the host molecules have identical *P* (or *M*) propeller chirality in the central ring, while the three distinct *sec*-butyl groups predominantly display an *RSR* (or *SRS*) configuration. The presence of the second diastereomer *RRR* (or *SSS*), anticipated to be present in low proportion, is not evident. Designating the three aromatic subunits A, B, and C, one sees no disorder in the B *sec*-butyl groups, which have the *R* configuration, while the A and C *sec*-butyl groups exhibit appreciable substitutional disorder: A has 0.8:0.2 *R*:*S* while C has 0.8:0.2 *S*:*R* occupancy values. Interestingly, the ordered *sec*-butyl group has an anti conformation, while both of the disordered ones have gauche conformations.[12] The guest is heavily disordered within the cavity, but separate atoms are discernable exhibiting 2-fold disorder that remains to be elucidated.

When single crystals of the TSBS clathrates are dissolved at 0 °C in chloroform, the solutions have initial optical rotations of $[\alpha]^{20}_{D}$ ~100° (some crystals afford (+) and some (−) rotation values), which over a period of 5 min approach 0°. This is due to the $P \rightleftharpoons M$ conformational isomerization of the propeller conformation of the host which, in single crystals of space group $P3_121$, should be homochiral.[13] The half-life ($\tau_{1/2}$) for this process was determined to be 4.7 min at 0 °C; on the basis of its temperature dependence (via polarimetry), the energy of activation ($\Delta G^{\ddagger}$) and Arrhenius parameters ($E_a$, log $A$) were calculated to be 22.2 and 22.7 kcal/mol and 16.1, respectively.

These results confirm that the structural motif of TOT may be modified in order to engineer improved host structures for clathrates and open up the possibility of obtaining host properties (e.g., chemical reactivity centers, optical properties for nonlinear effects, etc.) which are not observed in TOT. This is of specific importance and interest with regard to difficult resolutions (e.g., halothane) and may provide systematically modified clathrate structures which will allow us to better understand the structural requirements that lead to clathrate formation.

**Acknowledgment**. This research was supported by Grant No. 84-00162 from the U.S.–Israel Binational Science Foundation (BSF), Jerusalem, Israel, and The Research Corporation (RC4-45215). J.T.L. thanks NSF (R11-8504068) for a grant through the Visiting Professorship for Women program while at Brandeis. We thank Dr. S. Cohen for his valuable contributions.

**Supplementary Material Available:** Description of the data collection and tables of atomic coordinates, anisotropic temperature factors, hydrogen atom coordinates, bond lengths, and bond angles for the cage-type clathrate of TSBS (3) with (*S*)-(+)-2-butanol (10 pages). Ordering information is given on any current masthead page.

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(10) Edge, S. J.; Ollis, W. D.; Stephanatou, J. S.; Stoddart, J. F.; Williams, D. J.; Woode, K. A. *Tetrahedron Lett.* **1981**, *22*, 2229.

(11) Crystal data: $C_{36}H_{42}O_6 \cdot {}^1/_2(C_4H_{10}O)$, a transparent, prismatic, trigonal crystal, 0.4 mm in all dimensions was used; space group $P3_121$ (No. 152), $a = b = 13.556$ (2), $c = 31.705$ (8) Å, $Z = 6$, Fw = 607, $D_{calcd} = 1.10$ g cm$^{-3}$. Data collected at 90 K on a Rigaku AFC5R four circle diffractometer, RU300 rotating anode, load 40 KV, 250 mA, Mo K$\alpha$ radiation ($\lambda = 0.7114$ Å), graphite monochromator; 5630 reflections collected $2.0° \leq 2\Theta \geq 55.0°$; $\omega$ scan method, scan width = 1.0°, scan speed 1°/min; typical half-height peak width = 0.34° $\omega$; 3 standard reflections collected 55 times; no changes in intensity; no absorption correction; 3809 reflections with $I > 3\sigma(I)$. Solution and refinement: structure solved by direct methods (SHELXS-86). Anisotropic refinement for non-hydrogen atoms. Hydrogens were found from a difference Fourier map and refined constrained to regular geometry with an overall temperature factor. Scattering factors from International Tables of X-ray Crystallographic, Vol. IV. Prior to attempt to resolve disorder of the guest molecule, $R_w = 0.078$.

(12) For discussion and examples of *sec*-butyl group disorder, see: Addadi, L.; Ariel, S.; Lahav, M.; Leiserowitz, L.; Popovitz-Biro, R.; Tang, C. P. In *Chemical Physics of Solids and Their Surfaces*; Roberts, M. W., Thomas, J. M., Eds.; Royal Society of Chemistry: London, 1980; Vol 8, p 202.

(13) Although TOT and TSBS are very similar, the correlation of host sign of rotation with guest chirality is the *opposite* for their 2-butanol (BuOH) clathrates. (*S*)-(+)-2-BuOH is preferentially enclathrated by (−)-TSBS and (*R*)-(−)-2-BuOH is associated with (+)-TSBS, whereas (*S*)-(+)- and (*R*)-(−)-2-BuOH are exclusively associated with *P* (+)- and *M* (−)-TOT, respectively.[14]

(14) Burlinson, N. E.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3713.

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# Strongly Enhanced Stereoselectivity in the Reduction of 5-Substituted Adamantanones by Substitution of $C_5$ by Positive Nitrogen

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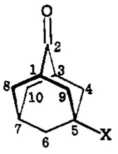
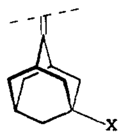
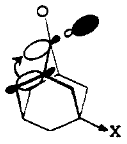
Studies of addition to the 5-substituted adamantanone **1-X** and its derivatives **2-X** have produced insights into the electronic factor influencing the stereochemistry of that process.[1] The results, highly uniform over a very wide variety of reactions,[2] appear to support the generalization that the reagent prefers attack at that face which is antiperiplanar to the more electron-rich vicinal bond(s). To interpret this phenomenon, we have employed the idea of transition-state hyperconjugation first proposed in 1981 by Cieplak[3] to explain the peculiar preference of many nucleophilic reagents for axial attack on cyclohexanone. Probes **2-X** have seemed ideal for these studies because from the steric point of view they have virtual $C_{2v}$ symmetry, and the donor bonds are essentialy strainless, yet rigidly oriented.



1-X



2-X



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Nevertheless, the concept has not been universally accepted, perhaps in part[4] because the selectivities in the reactions of electroneutral substrates **2-X** have been quite modest:[5] an *E*/*Z* alcohol ratio of about 1.5. Such small ratios make it difficult to dismiss the possible responsibility of a host of otherwise inconsequential factors; hence, we sought to design new probes possessing the same advantages of an adamantane skeleton but with a much more powerfully polarizing substituent. We now wish to report our findings in the borohydride reduction of 5-azaadamantan-2-one derivatives **4–6**. The known[6] parent amino ketone (**7**) is isoelectronic with **1-H**, and the configurations of the **E** and **Z** alcohols **8** derived from it have been determined.[7]

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(1) (a) Cheung, C. K.; Tseng, L. T.; Lin, M.-h.; Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 1598; **1987**, *109*, 7239. (b) Li, H.; le Noble, W. J. *Tetrahedron Lett.* **1990**, *31*, 4391.

(2) For a summary and references, see: Bodepudi, V.; le Noble, W. J. *J. Org. Chem.* **1991**, *56*, 2001.

(3) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540.

(4) For a summary and references, see: Wu, Y.-D.; Tucker, J. A.; Houk, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 5018.

(5) Much larger ratios ($10^{2-3}$) are encountered when the substrates are cations: (a) Srivastava, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 5874. (b) Xie, M.; le Noble, W. J. *J. Org. Chem.* **1989**, *54*, 3839. (c) Adcock, W.; Coope, J.; Shiner, V. J.; Trout, N. A. *J. Org. Chem.* **1990**, *55*, 1411.

(6) (a) Dekkers, W. J. D.; Verhoeven, J. W.; Speckamp, W. N. *Tetrahedron* **1973**, *26*, 1691. (b) Black, R. M. *Synthesis* **1981**, 829.

(7) Fernandez, M. J.; Galvez, E.; Lorente, A.; Iriepa, I.; Soler, J. A. *J. Heterocycl. Chem.* **1989**, *26*, 307. The assignments were based on a $^1$H NMR analysis of a mixture of 50/50 composition after purification. We succeeded in obtaining highly enriched samples of both alcohols by chromatography ($Al_2O_3$–methanol); we confirm their assignment.

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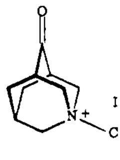

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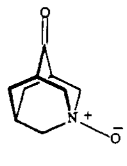

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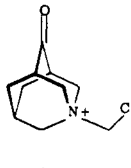

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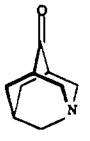

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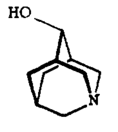
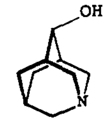


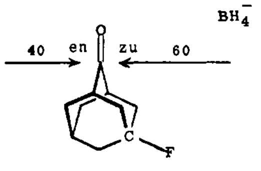
E-8

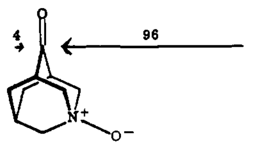


Z-8

The reduction of **4** in methanol gave a product whose NMR spectra suggested that it was a single compound. N-Methylation of the two parent alcohols **8**[7] showed the product to be the *E* epimer. Careful scrutiny of the base line in the NMR spectra revealed the *Z* alcohol to be detectible also, to the extent of 4–5%. Thus, the *E*/*Z* ratio of isomers in this instance was 20–25, an order of magnitude larger than any we had encountered before.

Oxidation of **7** gave amine oxide **5** (isoelectronic with our previously most powerful probe, **1**-F), and treatment of **7** with chloroacetic acid furnished betaine **6**. Both **5** and **6** were subjected to borohydride reduction and product proof and analysis, as was **4**; furthermore, $^{13}$C NMR additivity studies supported our assignments of configuration. The *E*/*Z* ratio in all three cases equaled 20–25.





One alternative reason for the large selectivity in **4** is the possibility of an electrostatic interaction bringing the borohydride anion preferentially to the *zu* face. Haberfield[8] has shown convincingly that such preassembly can lead to large rate effects, such as a factor of $10^6$ in one such reaction in THF, and also that the effect virtually vanishes (1.2) upon a change of solvent to water. In our case, the ratio with **4** did not change at all with a change of methanol to water or even to saturated aqueous sodium chloride. The results cannot be attributed to unexpected strains or distortions in the cage structure either. In support of this statement, we refer to Galvez's crystal structure of a derivative of protonated *E*-**8** ("Each ring of the adamantone cage system is a nearly perfect chair ...").[9a] A pyramidally distorted carbonyl group is ruled out by known crystal structures of monoprotonated[9b] and -methylated[9c] 5,7-diazaadamantanone, in which the three angles at C$_2$ add up to 360°. We conclude therefore that the unusually large selectivities reported here are attributable to transition-state hyperconjugation. The effect is so much more visible than before, because the bonds vicinal to the 5-substituent have been so much more powerfully deactivated.

The nucleophilic addition to **7** itself is also of interest, since it seems conceivable that the unshared pair on nitrogen might interact with the C$_{1-9}$ and C$_{3-4}$ bonds so as to promote their donor abilities. It is noteworthy, in this connection, to compare the following carbonyl stretching frequencies (KBr): **4**, 1735.5 cm$^{-1}$; **5**, 1729.0 cm$^{-1}$; adamantanone, 1718.2 cm$^{-1}$; **7**, 1713.4 cm$^{-1}$ (**6** gave only strong OH signals). Indeed, treatment with methyllithium in THF gave a mild excess (55–45) of the *Z* tertiary alcohol *Z*-**9**. Borohydride reduction in methanol produced an excess of *E*-**8** (62/38); possibly a hydrogen-bonded amine center is responsible for this unprecedented reversal of stereochemistry. We also mention here experiments detailed in the supplementary material and aimed at the pH dependence of the carbonyl carbon resonance of **7** and its derivatives. They may vary by more than 100 ppm; carbonyl hydration is responsible.[10,11]

**Acknowledgment.** We benefited greatly from advice and unpublished data by Professor Paul Haberfield of SUNY (Brooklyn) and from help in X-ray analysis by Professor Joe Lauher of our department. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

**Supplementary Material Available:** Synthesis and reduction experiments and physical properties of all new compounds mentioned in this report, as well as pertinent NMR spectra (24 pages). Ordering information is given on any current masthead page.

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(8) Haberfield, P.; Cincotta, J. J. *J. Org. Chem.* **1987**, *52*, 4627; **1990**, *55*, 1334.

(9) (a) Fernandez, M. J.; Galvez, E.; Lorente, A.; Soler, J. A.; Florencio, F.; Sanz, J. *J. Heterocycl. Chem.* **1989**, *26*, 349. (b) McCabe, P. H.; Milne, N. J.; Sim, G. A. *Acta Crystallogr.* **1989**, *C45*, 114. (c) Goncharov, A. V.; Panov, V. N.; Maleev, A. V.; Potekhin, K. A.; Kurkutova, E. N.; Struchkov, Y. T.; Palyulin, V. A.; Zefirov, N. S. *Dokl. Akad. Nauk USSR* (*Engl. Transl.*) **1991**, *318*, 148.

(10) Schulman, E. M.; Bonner, O. D.; Schulman, D. R.; Laskovics, F. M. *J. Am. Chem. Soc.* **1976**, *98*, S793. Van Luppen, J. J.; Lepoivre, J. A.; Dommisse, R. A.; Alderweireldt, F. C. *Org. Magn. Reson.* **1979**, *12*, 399.

(11) A referee suggested that we consider a recent critique (Frenking, G.; Kohler, K. F.; Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1146). In this computational paper, the authors state that the "explanation given by Cieplak ... is based on a rather paradoxical assumption: Stereoelectronic control ... is attributed to electron donation from the occupied orbitals ... into the vacant *antibonding* $\sigma^*$ orbital associated with the incipient bond" (italics theirs). Presumably, the explanation would not be "paradoxical" for a breaking bond yet, by virtue of microscopic reversibility, the transition states for bond formation and cleavage are the same. The explanation is paradoxical only if one attributes too literal a meaning to the term "antibonding". The proposition that electronic energy is lowered by delocalization into a vacant *orbital of higher energy* is a fundamental tenet of quantum chemistry.

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# Platinum-Mediated Reactions of Hydrosilanes. Isolation of a Complex with Bridging Disilene and Silylene Ligands

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Palladium and platinum provide the most widely used catalysts for transformations of organosilicon compounds.[1] Recent interest has focused on development of catalysts for the dehydrocoupling of hydrosilanes to polysilanes, which can suffer from competing, metal-catalyzed redistribution of substituents at silicon.[2] Unfortunately, enhancement of selectivity in these systems is complicated by a lack of relevant mechanistic information.[2c] Recent observations that Si–Si bond formation can occur via reductive elimination from Pt and Pd bis(silyl) complexes[2e,f] suggest the possibility that dehydrocoupling may occur simply via oxidative addition/reductive elimination cycles.[2c] Redistribution has most often been attributed to the activity of intermediate silylene complexes (e.g., (R$_3$P)Pt(=SiR′R″)(R‴)SiR′R″R‴),[2c] but oxidative addition/reductive elimination cycles could also account

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(1) (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 25, p 1479. (c) Tilley, T. D. In *The Silicon–Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York; Chapter 10, p 309. (d) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213 and references in the above.

(2) (a) Corey, J. In *Advances in Silicon Chemistry*; Larson, G., Ed.; JAI Press, Inc.: Greenwich, CT, 1991; Vol. 1., p 327. (b) Harrod, J. F.; Mu, Y.; Samuel, E. *Polyhedron* **1991**, *10*, 1239. (c) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37. (d) Laine, R. M. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Kluwer Academic Publishers: Amsterdam, 1990; p 37. (e) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411. (f) Schubert, U.; Müller, C. *J. Organomet. Chem.* **1989**, *373*, 165.