Transfer of Hydrogen from Orthoamides. Reduction of Protons to Molecular Hydrogen

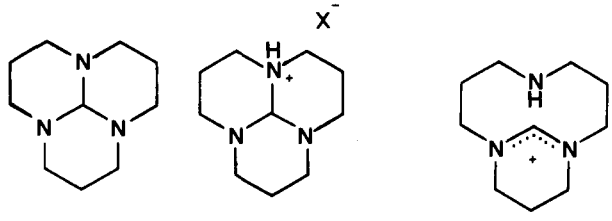
Sir:

The chemistry of simple alkanes is rich and complex.[1] One familiar but still puzzling reaction is the conversion of alkanes into carbenium ions by the action of superacids.[1,2] Two plausible mechanisms account for this reaction: (1) One mechanism invokes protonation of the alkane, followed by loss of molecular hydrogen (eq 1).[1,2] This reaction seems thermodynamically feasible,[3] but

$$RH + H^+ \rightleftarrows RH_2^+ \rightleftarrows R^+ + H_2 \qquad (1)$$

oxidations of alkanes by superacids do not produce the required amount of hydrogen.[1,2] The deficit may result from interception of hydrogen or interception of the protonated alkane by components of the superacid.[2] Hydrogen can in fact reduce neat antimony pentafluoride to antimony trifluoride and hydrogen fluoride,[2] but under similar conditions it has no effect on solutions of antimony pentafluoride in hydrogen fluoride or fluorosulfonic acid.[2,4] (2) The other plausible mechanism involves direct oxidation of the alkane by Lewis acids like fluorosulfonic acid, sulfur trioxide, or antimony pentafluoride.[4c,5] The oxidation of cycloheptatriene by sulfur trioxide, for example, cleanly produces tropylium and sulfur dioxide, but no hydrogen.[4c] However, some of the direct oxidations attributed to Lewis acids may actually require Brönsted acids present as significant impurities.[2] Many previous investigations of alkane oxidation are therefore ambiguous, and do not justify the firm acceptance of either mechanism. Here we report an oxidation which unequivocally involves Brönsted acids.

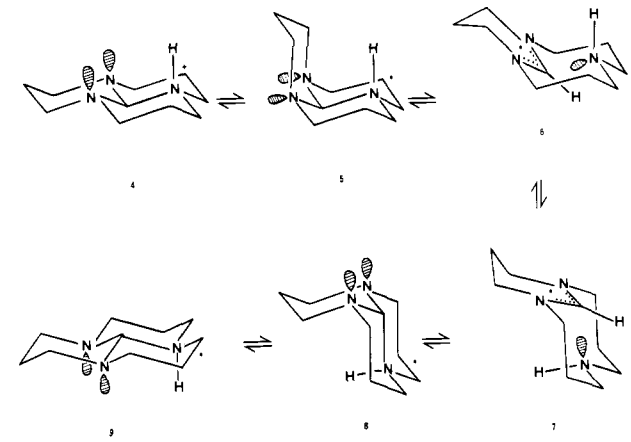
Treatment of perhydro-3a,6a,9a-triazaphenalene (**1**)[6] with equimolar amounts of aqueous tetrafluoroboric or hydrochloric acids yielded simple salts from which compound **1** could be re-



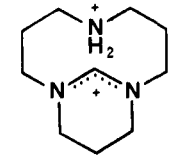
1 **2a** (X = BF_4) **2b** (X = Cl) **3**

generated by neutralization. Strong ammonium bands appeared in the infrared spectrum of the chloride in the solid state and in solution, and significant absorptions in the region 1500–2300 cm^{-1} were absent; thus the chloride adopts structure **2b**, not the alternative bicyclic structure **3**.[7,8] The infrared spectrum of the tetrafluoroborate was strikingly different. Prominent bands at 1660 and near 2900 cm^{-1} in the solid state and in solution were characteristic of neither the tricyclic structure **2a** nor the bicyclic structure **3**. Presumably the tetrafluoroborate adopts an intermediate structure incorporating a transannular donor–acceptor

Scheme I



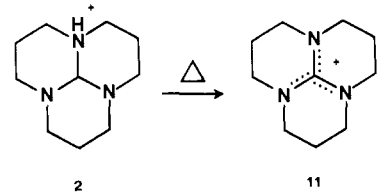
interaction.[9] The ^1H NMR spectra of both salts depended reversibly on temperature and at 70 °C in D_2O required in particular that chloride **2b** must possess the elements of effective D_{3h} symmetry [δ 2.26 (qn, 6 H), 3.39 (t, 12 H), 4.65 (s, 1 H)]. The equilibria described in Scheme I account for this observation. While not required by the appearance of the spectra, formation of intermediate **5** permits elimination of amine under stereoelectronic control.[10] The dynamic behavior of [7]metacyclophane[11] indicates that the ring inversion of formamidinium ions **6** and **7** should in fact be rapid near 25 °C. As we expected, addition of excess hydrochloric acid to orthoamide **1** precipitated bicyclic dichloride **10**.[7] Its infrared spectrum displayed strong bands characteristic of ammonium and formamidinium ions (1685 cm^{-1}),



10

but the ^1H NMR spectrum at 4 °C in D_2O [δ 2.14, (qn, 6 H), 3.48 (t, 12 H)] required a structure with the elements of effective D_{3h} symmetry. Structure **10** is consistent with this observation if ring inversion and reversible deprotonation are rapid at 4 °C.

The remarkably low stretching frequency of the central carbon–hydrogen bond in compound **1**[6b] promised that the orthoamide would show unusual reactivity. We were nevertheless very surprised to find that pyrolysis of solid tetrafluoroborate **2a** under nitrogen (110 °C, 23 h) cleanly produced guanidinium tetrafluoroborate **11**[6b] (eq 2). Hydrogen, the necessary byproduct,



2 **11** (2)

was captured quantitatively by *trans*-stilbene in the presence of 10% palladium on carbon. Boron trifluoride is not the effective oxidant in this reaction, since pyrolysis of chloride **2b** (170 °C, 12 h) similarly yielded guanidinium chloride **11**.[6b] Concerted elimination of molecular hydrogen is stereochemically impossible in ammonium salt **4** and thermally forbidden in isomer **12**; moreover, compound **12** is structurally similar to ammonium

(1) For a review, see: Brouwer, D. M.; Hogeveen, H. *Prog. Phys. Org. Chem.* **1972**, *9*, 179.
(2) Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* **1973**, *95*, 4960.
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(4) (a) Gillespie, R. J.; Pez, G. P. *Inorg. Chem.* **1969**, *8*, 1233. (b) Hogeveen, H.; Gaasbeek, C. J.; Bickel, A. F. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 703. (c) Larsen, J. W.; Bouis, P. A.; Watson, C. R., Jr.; Pagni, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 2284.
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(6) (a) Atkins, T. J. *J. Am. Chem. Soc.* accompanying paper. (b) Erhardt, J. M.; Grover, E. R.; Wuest, J. D. *Ibid.* accompanying paper.
(7) The assigned structure was consistent with the elemental analysis and the IR, NMR, and mass spectra of this new substance.
(8) We doubt that ammonium chloride **2b** adopts a tricyclic structure with C_{3v} symmetry.
(9) For references, see: Leonard, N. J. *Rec. Chem. Prog.* **1956**, *17*, 243. Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065. Birnbaum, G. I. *Ibid.* **1974**, *96*, 6165.
(10) Deslongchamps, P. *Tetrahedron* **1975**, *31*, 2463. *Pure Appl. Chem.* **1975**, *43*, 351.
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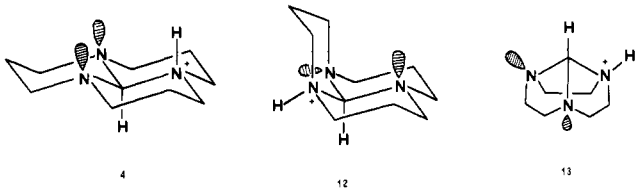
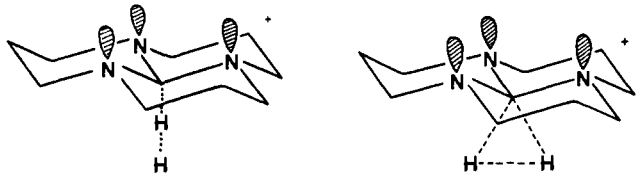


4 12 13

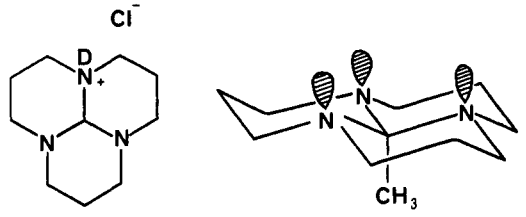
tetrafluoroborate **13**, which melted at 130 °C without decomposition.[12] As a result, we suggest that reaction 2 occurs in two steps: (1) dissociation of ammonium tetrafluoroborate **2a** into orthoamide **1** and tetrafluoroboric acid and then (2) oxidation of orthoamide **1** by the Brønsted acid. Protonation of the central carbon–hydrogen bond of the orthoamide can produce a transition state or intermediate with either the linear configuration **14** or the triangular configuration **15**.[1,2] Although structure **15** assumes



14 15

the C_s symmetry favored by protonated methane,[13] it is destabilized by nonbonded interactions on the protonated face of the molecule.[14] We tentatively favor structure **14** for an additional reason. The direct exchange of hydrogen with superacids (eq 3) is a characteristic reaction of alkanes which is invariably faster than oxidation.[1,2] Structures like carbonium ion **15** readily accommodate this rapid exchange. In contrast, formation of linear ion **14** followed by a virtually irreversible loss of molecular hydrogen would permit oxidation without exchange. In fact, oxidation of orthoamide **1** is much faster than the exchange of hydrogen; orthoamide **1** recovered after partial conversion of deuterioammonium chloride **16** to guanidinium chloride **11** (175 °C, 1 h, $CDCl_3$) contained deuterium in only normal abundance.

$$RD + H^+ \rightleftarrows RH + D^+ \quad (3)$$



16 17

Our results demonstrate unambiguously that the proton can oxidize activated alkanes. Since this particular oxidation requires Brønsted acids of only moderate strength, and since it occurs faster than the exchange of hydrogen, the central carbon–hydrogen bond of orthoamide **1** must be extraordinarily reactive. Mixing of σ_{CH}* with three antiperiplanar lone-pair orbitals accounts for this remarkable activation.[6b] During the reductions of triphenylcarbenium and methyl phenyl glyoxylate by orthoamide **1**, however, the central carbon–hydrogen bond is not broken.[6b] Our present results suggest that this bond is sufficiently reactive, but not readily accessible to bound substrates. They also indicate that if carbon–carbon bonds can be similarly activated, orthoacetamide **17** should transfer methyl with special facility.

(12) Grover, E. R.; Wuest, J. D., unpublished results.
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Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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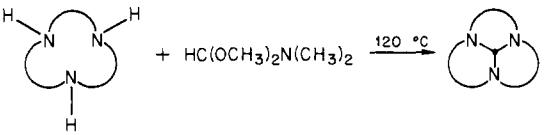
Received December 26, 1979

Tricyclic Trisaminomethanes

Sir:

Recent reports from these laboratories have described the synthesis of macrocyclic polyamines[1] and their use in preparing novel polycyclic compounds via an "insertion" reaction, forming three of four bonds to the macrocycle ring.[2] We have found that the macrocyclic cage imparts high stability and unusual reactivity to the central moiety of those systems reported. Although this "macrocyclic effect" has long been recognized and utilized in transition-metal chemistry, it has not been fully exploited by organic chemists. On the basis of examination of models, stable polycyclic trisaminomethanes could be prepared via an exchange reaction and should exhibit novel reactivity dependent on the ring size of the starting macrocycle.

The uncatalyzed exchange reaction between ethyl orthoformate and macrocyclic triamines was unsuccessful. However, when the more reactive dimethylformamide dimethyl acetal was substituted for orthoformate, the exchange reaction (eq 1) proceeded smoothly



(1)

to give the polycyclic trisaminomethanes listed in Table I *in high yield*. The reaction was run with stoichiometric amounts of reactants, either neat or in the presence of inert solvent.[3]

The structures **1–7** were assigned on the basis of their spectral properties and elemental analyses.[4] For example, the 220-MHz ^1H NMR spectrum of **1** exhibited an AA'BB' pattern for the methylene hydrogens. Computer simulation of the pattern gave coupling constants consistent with the expected eclipsed conformation.[5] Compounds **2–6** also exhibited ^1H NMR spectra consistent with their assigned structures.[5]

Apparently anomalous NMR spectra were observed for **7** at room temperature. The methylene protons appeared as a singlet,[5,6] and the hydrogen-decoupled ^{13}C NMR spectrum in CD_2Cl_2 exhibited only two absorptions, δ 101.1 (methine C) and 52.8 (methylene C). However, low-temperature analysis of the 220-

(1) J. E. Richman and T. J. Atkins, *J. Am. Chem. Soc.*, **96**, 2268 (1974); T. J. Atkins, J. E. Richman, and W. F. Oettle, *Org. Synth.*, **58**, 86 (1978).
(2) (a) J. E. Richman and H. E. Simmons, *Tetrahedron*, **30**, 1769 (1974); (b) J. E. Richman, *Tetrahedron Lett.*, 559 (1977); (c) T. J. Atkins, *ibid.*, 4331 (1978); (d) T. J. Atkins and J. E. Richman, *ibid.*, 4333 (1978); (e) *ibid.*, 5149 (1978).
(3) U. S. Patents 4085106 and 4130715.
(4) Elemental analyses within 0.4% of theory were obtained on all new compounds.
(5) 220-MHz ^1H NMR spectra of the methylene region. **1**: δ 3.08 (6 H, AA', J_{AB} = −10.9 Hz, $J_{AA'} = J_{AB'}$ = 5.9 Hz), 2.80 (6 H, BB', $J_{BB'}$ = 6.1 Hz). **2**: δ 3.35 (2 H, octet), 3.17 (2 H, octet), 3.06–2.91 (4 H, m), 2.79 (2 H, octet), 2.63 (2 H, octet), 1.97 (1 H, dp), 1.09 (1 H, dp). **3**: δ 3.20 (2 H, q), 2.99 (2 H, m), 2.80 (2 H, m), 2.51 (2 H, q), 2.39 (2 H, m), 1.98 (4 H, m), 1.43 (2 H, m). **4**: δ 2.82 (6 H, m), 2.23–1.92 (9 H, m), 1.43 (3 H m). **5**: δ 3.36–2.32 (8 H, m), 2.30 (6 H, s). **6**: δ 3.95 (2 H, m), 3.56 (2 H, m), 3.15 (2 H, m), 3.06 (2 H, m), 2.88 (2 H, m), 2.84–2.71 (4 H, m), 2.64 (2 H, m). **7**: δ 2.90 (16 H, s), 1.54 (1 H, br s) at 100 MHz. Detailed NMR and conformational analyses will be reported in a full paper.
(6) At 100 MHz in C_6D_6, the methylene absorption was δ 2.75, $w_{1/2}$ = 9 Hz. At 220 MHz in $CFCl_3$, they appeared at δ 2.85.

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