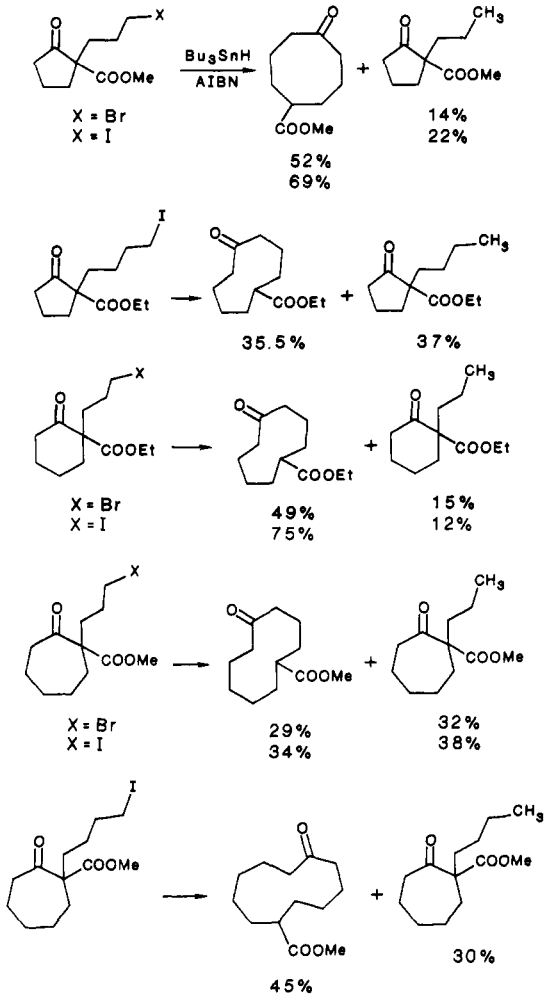
Table I. Three- and Four-Carbon Ring Expansion of β-Keto Esters[a,b]

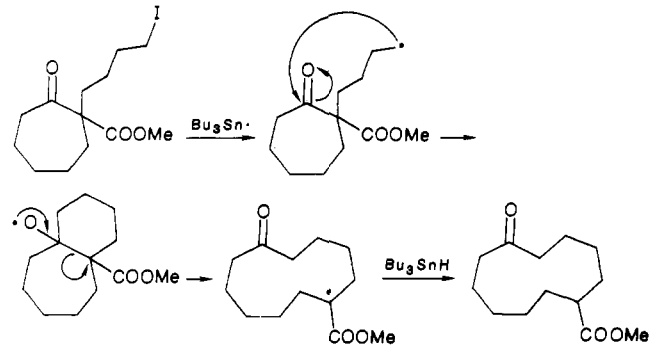


[a] All new substances had satisfactory carbon-13 and proton NMR, IR, and mass spectra. [b] % isolated yields.

In the one-carbon ring expansion described earlier,[2-4] there were two possible reaction paths. The reaction could have proceeded by addition of the primary radical to the ketone carbonyl[7] followed by fragmentation–ring enlargement of the oxy radical, as we had (tentatively) formulated the mechanism.[2] Alternatively, the primary radical might have fragmented to an acyl radical and an acrylate.[8] The reaction would be completed by addition of the acyl radical to the β-carbon of the acrylate. Of these two mechanistic alternatives the fragmentation pathway is untenable in the present work. A possible mechanism is suggested in Scheme I.

Since Beckwith[9] has shown that treatment of 2-(4-bromobutyl)cyclohexanone with tri-*n*-butyltin hydride yields little or no ring expansion product, it is clear that the ester plays a critical

Scheme I



role in the rearrangement described above, perhaps in activating the ketone and certainly in providing a driving force for the ring expansion.

To summarize, we have described a novel method to enlarge the normal 5-, 6-, and 7-membered β-keto esters in a strictly regioselective reaction to the more difficultly accessible 8-, 9-, 10-, and 11-membered rings.[10]

Acknowledgment. This research was generously supported by Institute of General Medical Sciences of the National Institutes of Health under Grant GM 19906.

(6) Cf. Porter et al. (Porter, N. A.; Magnin, D. R.; Wright, B. T. *J. Am. Chem. Soc.* **1986**, *108*, 2787) where the free radical cyclization of alkyl iodides on unsaturated ketones was very effectively used in the synthesis of medium and large rings.

(7) Competitive addition to carbonyl groups and double bonds has recently been examined by Tsang et al. (Tsang, R.; Dickson, J. K., Jr.; Pak, H.; Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1987**, *109*, 3484). See, also: Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 8102. Nickon, A.; Iwadare, T.; Maguire, F. J.; Mahajan, J. R.; Narang, S. A.; Umezawa, B. *J. Am. Chem. Soc.* **1970**, *92*, 1688. Spero, G. B.; Thompson, J. L.; Schneider, W. P.; Kagan, F. *J. Org. Chem.* **1963**, *28*, 755. Suginome, H.; Sato, N.; Masumune, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 215. Suginome, H.; Sato, N.; Masumune, T. *Tetrahedron Lett.* **1967**, 1557. Heusler, K.; Kalvoda, J. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 525.

(8) Cf. Riemann, H.; Capomaggi, A. S.; Strauss, T.; Oliveto, E. P.; Barton, D. H. R. *J. Am. Chem. Soc.* **1961**, *83*, 4481.

(9) Beckwith, A. L. J.; Kazlauskas, R.; Syner-Lyons, M. R. *J. Org. Chem.* **1983**, *48*, 4718. We thank Professor Dennis P. Curran for this reference.

(10) **Added in Proof**: We have recently learned in a private communication from Professor A. L. J. Beckwith that he has also observed free radical mediated insertion of three and four carbons in cyclic β-keto esters.

A Receptor for the Oriented Binding of Uric Acid Type Molecules

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Received May 11, 1987

Host–guest chemistry to date has focussed primarily on binding interactions which involve at least one charge-bearing partner (e.g., metal and alkylammonium ions).[1] With rare exceptions,[2a-e] those

(1) Among recent *leading* references see: (a) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1039–1057. (b) Colquhoun, H. M.; Stoddart, J. F.; Williams D. J. *Ibid.* **1986**, *25*, 487–507. (c) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *New Scientist* **1986**, *110* (1 May), 44–48. (d) Vögtle, F.; Löhr, H.-G.; Franke, J.; Worsch, D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 727–742. (e) Lehn, J. M. *Science (Washington, D.C.)* **1985**, *227*, 849–856. (f) Breslow, R. *Adv. Enzymol.* **1986**, *58*, 1–60. (g) Shepodd, T. J.; Petti, M. A.; Dougherty, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 6085–6087. (h) Bell, T. W.; Firestone, A. *Ibid.* **1986**, *108*, 8109–8111. (i) van Staveren, C. J.; Fenton, D. E.; Reinhoudt, D. N.; van Eerden, J.; Harkema, S. *Ibid.* **1987**, *109*, 3456–3458.

(2) (a) Rebek, J., Jr.; Askew, B.; Islam, N.; Killoran, M.; Nemeth, D.; Wolak, R. *J. Am. Chem. Soc.* **1985**, *107*, 6736–6738. Rebek, J., Jr.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *Ibid.* **1985**, *107*, 7476–7481. Rebek, J., Jr.; Nemeth, D. *Ibid.* **1986**, *108*, 5637–5638. Rebek, J., Jr.; Askew, B.; Ballester, P.; Buhr, C.; Jones, S.; Nemeth, D.; Williams, K. *Ibid.* **1987**, *109*, 5033–5035. Rebek, J., Jr. *Science (Washington, D.C.)* **1987**, *235*, 1478–1484. (b) Feibush, B.; Figueroa, A.; Charles, R.; Onan, K. D.; Feibush, P.; Karger, B. L. *J. Am. Chem. Soc.* **1986**, *108*, 3310–3318. (c) Hine, J.; Ahn, K.; Gallucci, J. C.; Linden, S.-M. *Ibid.* **1984**, *106*, 7980–7981. (d) Sheridan, R. E.; Whitlock, H. W., Jr. *Ibid.* **1986**, *108*, 7120–7121. (e) Hamilton, A. D.; Engen, D. V. *Ibid.* **1987**, *109*, 5035–5036. For less oriented binding of neutral guests in nonaqueous solvents see, inter alia: (f) Jarvi, E. T.; Whitlock, H. W. *Ibid.* **1982**, *104*, 7196–7204. (g) Bauer, L. J.; Gutsche, C. D. *Ibid.* **1985**, *107*, 6063–6069. (h) O'Krongly, D.; Denmeade, S. R.; Chiang, M. Y.; Breslow, R. *Ibid.* **1985**, *107*, 5544–5545. (i) Mosier-Boss, P. A.; Popov, A. I. *Ibid.* **1985**, *107*, 6168–6174. (j) Menger, F. M.; Dulany, M. A. *Tetrahedron Lett.* **1985**, *26*, 267–270. (k) Canceill, J.; Lacombe, L.; Collet, A. *J. Am. Chem. Soc.* **1986**, *108*, 4230–4232. (l) Ferguson, S. B.; Diederick, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1127–1129. (m) Lutter, H.-D.; Diederick, F. *Ibid.* **1986**, *25*, 1125–1127. (n) Aarts, V. M. L. J.; van Staveren, C. J.; Grootenhuis, P. D. J.; van Eerden, J.; Kruise, L.; Harkema, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1986**, *108*, 5035–5036, and ref 1a.

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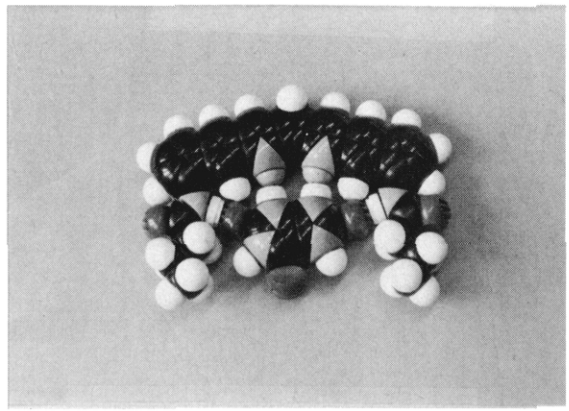
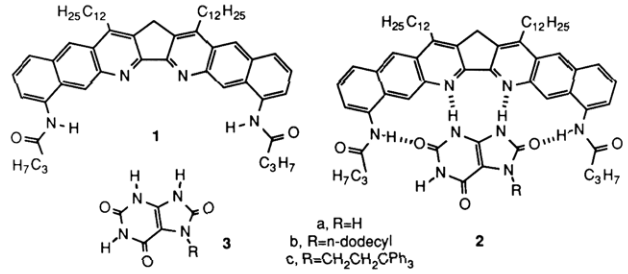


Figure 1. CPK model of **2a** (minus dodecyl groups).

relatively few systems which consist of only neutral components and operate in nonaqueous solvents[2] do not impose upon the guest a specific orientation once it is positioned within the binding site of the receptor. The control of such alignment would appear central to the development of efficient synthetic enzymes.[3] In the present communication we describe a system, intended for use in organic solvents, which not only constrains the guest to a particular position with respect to the host but also illustrates the substantial enhancement of binding affinity which can attend the use of relatively rigid receptors. The results also suggest some limitations in the use of CPK models.

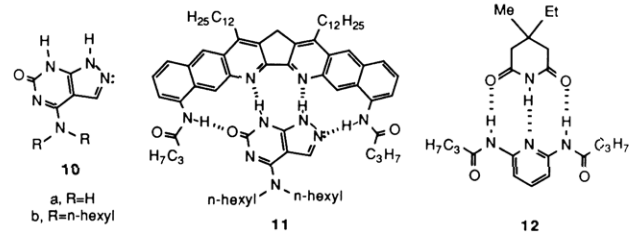
Receptor **1** was designed to recognize and bind (→**2**) uric acid (**3a**); CPK models indicated (see Figure 1) that a good fit should obtain. Preparation of **1** in useful (gram) quantities was achieved



as outlined in Scheme I; the synthesis is materially facilitated by the finding that unstable **7** can be trapped in situ with **5**, affording the seven-ring assembly **8** directly from tricycle **6** in 53% yield.[6]

Uric acid itself (**3a**) proved too insoluble in neutral organic solvents to determine if binding with **1** occurs. The *N*-dodecyl uric acid (**3b**), prepared from alloxantin by conventional[7] methods, is sufficiently soluble to allow binding studies in DMSO but not in less polar solvents. No evidence of binding of **3b** by **1** was observed ($K_{dissoc} \leq 10^{-2}$ could have been detected). While the potential of DMSO to compete as a hydrogen bond acceptor provided a possible explanation for the apparent absence of binding (→**2b**), reexamination of the design of **2** suggested a possible flaw: normal CPK hydrogen bonds had been employed in the engineering of **2**, but consideration of finer points of molecular detail revealed that the CPK hydrogen bond is only 2.69 Å long,[8] whereas a length of ~2.9–3.0 Å for the two N—H···O=C hydrogen bonds seemed more appropriate.[9,2b] Thus, the jaws of **1** are ~0.5 Å (2 × ~0.25 Å) too narrow. Superposition of the known[10] (X-ray) dimensions of uric acid on the calculated[11] dimensions of **1** reinforced that conclusion.

For the purpose of testing the underlying design concepts, it was easier to change the guest than the host. The pyrazolo[3,4-*d*]pyrimidone system **10** is one atom shorter (the =O) than



uric acid but retains the four hydrogen bonding sites. Commercially available[12] **10a** is, again, too insoluble, but its *N*,*N*-di-*n*-hexyl derivative **10b**[13] exhibits satisfactory solubility in low polarity solvents.

The affinity of **1** for **10b** is gratifyingly strong: K_{dissoc} for complex **11** = 1.1 × 10^{-6} M (±19%)[14] in 1:1 (v/v) CH_2Cl_2/toluene; for comparison, K_{dissoc} of **12**[2b] is[15] 8 × 10^{-3} M. That binding in **11** occurs with the orientation shown is corroborated by changes (and lack of changes) in ^{1}H NMR chemical shifts which attend binding of **1** with **10b**.

The use of solvents that do not compete effectively as hydrogen bonding partners appears crucial to good binding. No binding of **10b** with **1** is observed ($K_{dissoc} \leq 10^{-2}$ could have been detected) in either DMSO or dioxane; also, addition of MeOH to a $CHCl_3$ solution of **11** results in instantaneous disruption of the complex.

Notwithstanding the argument above that the jaws of **1** are too narrow to accommodate the uric acid contour, it still seemed desirable to definitively assess that judgment experimentally. A soluble uric acid derivative was eventually found in **3c**.[16] Contrary to expectations, **1** binds **3c** tightly: K_{dissoc} for complex **2c** = 1.0 × 10^{-6} M (±26%) in 1:1 CH_2Cl_2/toluene.[14]

It would thus appear that although the relative rigidity of **1** contributes to the very strong binding of **10b** and **3c**, rigidity is not so exacting in terms of precise topographical complementarity as might have been anticipated.[17] Whether **1**'s tight binding of

(3) For potential applications see, inter alia: Drexler, K. E. *Engines of Creation*; Anchor Press/Doubleday: Garden City, New York, 1986.

(4) Meals, R. N. *J. Org. Chem.* **1944**, 9, 211–218. Use of lithium containing 1% sodium is necessary.

(5) Coone, C. L.; Bluche, G. W.; Hill, M. E. *J. Org. Chem.* **1973**, *38*, 4243–4248.

(6) For the synthesis of somewhat related compounds, see: Thummel, R. P.; Lefoulon, F.; Williamson, D.; Chavan, M. *Inorg. Chem.* **1986** *25*, 1675–1679, and references therein.

(7) Fischer, E. *Chem. Ber.* **1897**, *30*, 559–573. Piloty, O. *Liebigs Ann. Chem.* **1904**, *333*, 22–71.

(8) Hart, R. A. *Molecules in Three Dimensions: A Guide to the Construction of Biologically Interesting Molecules with CPK Models*; American Society of Biological Chemists: Bethesda, MD, 1969; p 16.

(9) Vinogradov, S. N.; Linnell, R. H. *Hydrogen Bonding*; Van Nostrand Reinhold: New York, 1971; p 177. See also ref 2b.

(10) Ringertz, H. *Acta Crystallogr.* **1966**, *20*, 397–403.

(11) Trigonometric (not energy minimization) calculations were performed by using the Macintosh program *Molecular Editor* (Smith, A. L., Drexel University; available through Kinko's Graphics Academic Courseware Exchange, Santa Barbara, CA) and X-ray determined bond lengths/bond angles for, inter alia, fluorene (Burns, D. M.; Iball, J. *Proc. Roy. Soc. A* **1955**, *227*, 200–214), acridine (Phillips, D. C.; Ahmed, F. R.; Barnes, W. H. *Acta Crystallogr.* **1960**, *13*, 365–377), anthracene (Cruickshank, D. S. *Ibid.* **1956**, *9*, 915–923), and phenanthrene (Trotter, J. *Ibid.* **1963**, *16*, 605–608).

(12) Aldrich, listed (incorrectly) as 4-amino-6-hydroxypyrazolo[3,4-*d*]-pyrimidine.

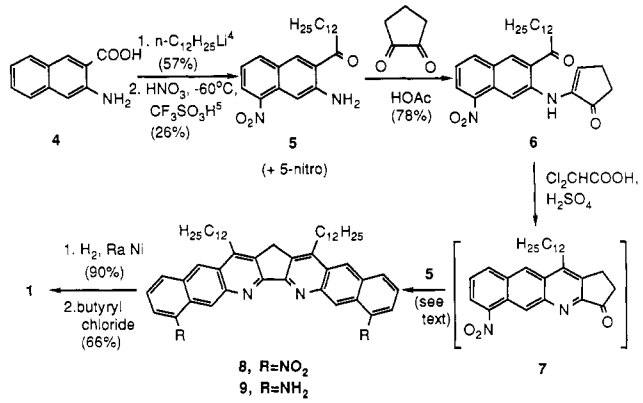
(13) Prepared from 4,6-dichloropyrazolo[3,4-*d*]pyrimidine (Robins, R. K. *J. Am. Chem. Soc.* **1957**, *79*, 6407–6415) by reaction with di-*n*-hexylamine followed by hydrolysis.

(14) (a) In alcohol-free $CHCl_3$ π-stacking of **11** appears to occur; it is apparently disrupted by toluene. (b) Binding was measured by monitoring the shift from 393 to 400 nm (393 to 401.5 nm with **3c**) in the UV absorbance of solutions 2.0 × 10^{-5} M in **1** brought about by including 0.20, 0.50, 0.75, 1.0, 2.0, 5.0, and 10.0 equiv of **10b**. Binding constants were extracted by the mole ratio method (cf.; Skoog, D. A.; West, D. M. *Fundamentals of Analytical Chemistry*, 4th ed.; Saunders: Philadelphia, 1982; p 553).

(15) Kelly, T. R.; Maguire, M. P.; Bell, S. H., unpublished results.

(16) Prepared[7] from alloxantin and β-tritylethylamine (**i**); **i** was obtained by $LiAlH_4/AlCl_3$ reduction of β,β,β-triphenylpropionitrile (Schorr, M. *Liebigs Ann. Chem.* **1963**, *661*, 157–164).

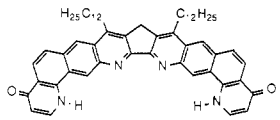
Scheme I



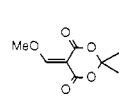
10b and **3c**, which are, respectively, ~0.7 Å too short and ~0.5 Å too long for a "perfect" fit indicates (i) that hydrogen bond lengths are more adaptable than expected, (ii) that binding of **10b** and **3c** induces changes in the shape of **1** (the two N-H's of **1** can be regarded as being at the extremes of two long lever arms extending from a central fulcrum), or (iii) that in complex **2c**, **3c** is tilted[18] relative to the plane of **1** are questions which remain unanswered. X-ray crystallography of complexes **2c** and **11** would shed light on these questions, but, despite considerable effort,[19] neither **2c** nor **11** has yet been induced to crystallize. Further studies are in progress.[20]

Acknowledgment. We thank Dr. S. H. Bell for the preparation of **3c** and other contributions, Professor E. J. Billo for assistance with determination of binding constants, and Professors E. R. Kantrowitz, L. W. McLaughlin, D. J. Sardella, K. D. Onan[2b] (Northeastern), and R. P. Thummel[6] (Houston) for helpful consultations.

(17) Indeed, the modicum of flexibility [e.g., rotation around the Ar-butyramide bond] incorporated in **1** may be advantageous: **i**, the very rigid nine-ring nominal isostere of **1**, exhibits no detectable binding with either **10b** or **3c** in either DMSO or 1:1 (v/v) CH_2Cl_2/toluene (because of the poor solubility of **i** only $K_{dissoc} \leq \sim 10^{-3}$ could have been detected with CH_2Cl_2/toluene). Compound **i** was prepared by condensation (50%) of **9** with **ii** followed by cyclization (44%) in refluxing diphenyl ether (Cassis, R.; Tapia, R.; Valderrama, J. A. *Synth. Commun.* **1985**, *15*, 125-133).



i



ii

(18) For a study of the directionality of hydrogen bonds, see: Taylor, R.; Kennard, O.; Versichel, W. *J. Am. Chem. Soc.* **1983**, *105*, 5761-5766. Hydrogen bonds tolerate modest deviations from linearity: Fersht, A. *Enzyme Structure and Mechanism*, 2nd ed.; W. H. Freeman: New York, 1985; p 297.

(19) Complex **11** is more soluble in nonpolar solvents than its constituents, presumably (in part) because binding attenuates the polarity of the four hydrogen bonding sites present in both **1** and **10b**. Thus, addition of hexane to a $CHCl_3$ solution of **11** results in desolubilization of **1** and/or **10b**; as noted above, addition of MeOH to a $CHCl_3$ solution of **11** disrupts the complex.

(20) All compounds gave spectral data in agreement with the structures assigned; satisfactory combustion analyses were obtained for most new compounds. ^1H NMR data and [mp's] for selected compounds: **1** [224-227 °C, dec] δ ($CDCl_3$) 0.87 (6 H, t, J = 6.8), 1.15-1.48 (38 H, m), 1.57 (4 H, m), 1.78 (4 H, m), 1.98 (4 H, m), 2.68 (4 H, br t, J = 7.5), 3.18 (4 *H*, br t, J = 7.5), 3.97 (2 H, s), 7.28 (2 H, br apparent t, J ~8.2), 7.64 (2 H, br d, J = 8.4), 8.08 (2 H, br d, J = 8.1), 8.15 (2 H, br s), 8.32 (2 H, s), 9.00 (2 H, s); **3c** [170~180 °C, dec] δ (DMSO-d_6) 2.91 (2 H, m), 3.42 (2 H, m), 7.17-7.41 (15 H, m), 10.78 (1 H, br s), 11.75 (2 H, br s); **5** [110-111 °C] δ ($CDCl_3$) 0.88 (3 H, t, J = 6.9), 1.22-1.48 (18 H, m), 1.78 (2 H, apparent pentet, J = 7.2), 3.11 (2 H, t, J = 7.4), 6.35 (2 H, br s), 7.20 (1 H, t, J = 7.8), 7.88 (1 H, br s), 8.00 (1 H, br d, J = 7.8), 8.35 (1 H, dd, J = 7.8, 1.2), 8.40 (1 H, br s); **8** [189-191 °C] δ ($CDCl_3$) 0.86 (6 H, t, J = 6.8), 1.20-1.42 (32 H, m), 1.46-1.58 (4 H, m), 1.64-1.76 (4 H, m), 3.11 (4 H, br t, J = 7.5), 4.13 (2 H, br s), 7.39 (2 H, dd, J = 8.1, 7.5), 7.94 (2 H, br d, J = 8.1), 8.09 (2 H, s), 8.30 (2 H, dd, J = 7.5, 1.2), 9.48 (2 H, s); **10b** [269-271 °C] δ ($CDCl_3$) 0.89 (6 H, m), 1.24-1.48 (12 H, m), 1.73 (4 H, m), 3.58 (2 H, br t, J = 7.2), 3.80 (2 H, br t, J = 7.2), 7.72 (1 H, s), 12.14 (1 H, br s), 14.85 (1 H, br s).

The First Practical Niobium(III) Reagent in Organic Synthesis. A Convenient Route to 2-Amino Alcohols via the Coupling of Imines with Aldehydes or Ketones Promoted by $NbCl_3$(DME)

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Received June 5, 1987

The application of low-valent early transition metals as two electron reductants in organic synthesis has centered around titanium and zirconium complexes,[1] with recent attention being focused on the metallocene derivatives of these metals (i.e., "Cp_2Ti"[2] and "Cp_2Zr"[3] which are generated in situ by reduction of the corresponding Cp_2MX_2). We have been interested in using $Nb(III)Cl_3L_n$ reagents with the anticipation that such species should exhibit markedly different reaction chemistry from the group IV metallocenes. These differences would arise from the enhanced Lewis acidity of the niobium-chloride complexes and the potential for substitution of the chlorides with other ligands (e.g., chiral ligands). Prior to this work the primary soluble sources of "$NbCl_3$" were the well-known series of dimers, $Nb_2Cl_6L_3$[4] (e.g., L = tetrahydrothiophene (THT), Me_2S, Cl^-), which have exhibited a rich inorganic and organometallic chemistry.[5] However, large scale syntheses of these materials (e.g., >50 g) are not convenient for practical applications in stoichiometric organic reactions. Herein, we report a new and convenient synthesis of 2-amino alcohols via the cross coupling of an imine with an aldehyde or ketone by using a readily available niobium reagent, $NbCl_3$(DME) (**1**).

$NbCl_3$(DME) (**1**) is prepared by the addition of $NbCl_5$ to a solution of tributyltin hydride in dimethoxyethane (DME) at -78 °C (eq 1).[6] The $NbCl_3$(DME) precipitates from the reaction

$$NbCl_5 + 2\,Bu_3SnH \xrightarrow{DME} NbCl_3(DME) + 2\,Bu_3SnCl + H_2 \quad (1)$$

allowing for easy separation from the tributyltin chloride that is generated. The isolated brick-red solid is then simply stored (under an inert atmosphere) and used when desired. At this time, we do not know the molecular structure of **1** due to its lack of solubility in any solvent with which it does not react. The *empirical* formula shown is based on repeated elemental analyses[7] and the reaction of **1** with tetrahydrothiophene which produces the known complex $Nb_2Cl_6(THT)_3$ in high yield (88%). No hydrogen was evolved from this reaction indicating that **1** is not a niobium(IV) hydride.

(1) For reviews, see: (a) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405. (b) Seebach, D.; Weidmann, B.; Widler, L. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Wiley: New York, 1983; Vol. 3. (c) Lai, Y. H. *Org. Prep. Proc. Int.* **1980**, *112*, 361. (d) Ho, T. L. *Synthesis* **1979**, 1.

(2) (a) Nugent, W. A.; Thorne, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788 and references therein. (b) Famili, A.; Farona, M. F.; Thanedar, S. *J. Chem. Soc., Chem. Commun.* **1983**, 435.

(3) (a) See ref 2a. (b) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1987**, *28*, 917. (c) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Ibid.* **1986**, *27*, 2829. (d) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568.

(4) (a) Allen, A. D.; Naito, S. *Can. J. Chem.* **1976**, *54*, 2948. (b) Maas, E. T., Jr.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1096.

(5) For examples, see: (a) Cotton, F. A.; Diebold, M. P.; Matusz, M.; Roth, W. J. *Inorg. Chim. Acta* **1986**, *112*, 147. (b) Cotton, F. A.; Diebold, M. P.; Llusar, R.; Roth, W. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1276. (c) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 3509. (d) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 6987. (e) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Ibid.* **1984**, *106*, 4749. (f) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Ibid.* **1984**, *106*, 3527. (g) Cotton, F. A.; Roth, W. J. *Inorg. Chim. Acta* **1984**, *85*, 17. (h) Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233.

(6) For other examples where Bu_3SnH has been used to reduce an inorganic halide, see: (a) Roskamp, E. J.; Pedersen, S. F. *J. Am. Chem. Soc.* **1987**, *109*, 3152 (Supplementary Material). (b) Roth, A.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1986**, *108*, 6823. (c) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

(7) Anal. Calcd for $NbC_4H_{10}Cl_3O_2$: C, 16.60; H, 3.48; Cl, 36.76. Found: C, 16.94; H, 3.71; Cl, 36.65; N, 0.00 (average of six separate analyses on three different samples). See Supplementary Material for further details.

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