The form of eq 1 used here emphasizes that f and g function as the effective interaction strength and asymmetry parameter, respectively.

The "static" quadrupole coupling constant e^2qQ/h and asymmetry parameter η were determined from spectra of 8-deuterated adenosine and guanosine,[13] whose spin-lattice relaxation times exceed 5 s and therefore serve as suitably rigid reference materials. By inserting $e^2qQ/h = 179 \pm 1$ kHz and $\eta = 0.06 \pm 0.01$ as well as the transition frequencies for $\beta = 0°$ ($\nu = 69.3 \pm 0.7$ kHz) and $\beta = 90°$, $\gamma = 90°$ ($\nu = 59.8 \pm 0.6$ kHz) into eq 1-3, we estimate the librational amplitudes $\phi_0 = 13 \pm 2°$ and $\theta_0 = 10 \pm 2°$ for the B-form Li-DNA (Figure 1B). These amplitudes, while necessarily model-dependent, are rather insensitive to the precise form of the librational potential.

The deuteron spectra of dehydrated Li-DNA do not exhibit such signs of motional narrowing and $T_1 > 5$ s. In contrast, we find that $T_1 = 80$ ms at 38 MHz for Li-DNA at 75% relative humidity. The analysis presented above demonstrates that the much shorter T_1 is due to motions of limited amplitude but with significant spectral density in the Larmor frequency range. Preliminary relaxation measurements at 76 MHz show that T_1 is frequency-dependent and the determination of individual spectral densities of motion using techniques developed previously for liquid crystals[13] is currently in progress in our laboratory.

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(13) Tsang, P.; Vold, R. R.; Vold, R. L.; Kearns, D. R., unpublished results.

A Catalytic Tin System for Trapping of Radicals from Cyclization Reactions. Regio- and Stereocontrolled Formation of Two Adjacent Chiral Centers

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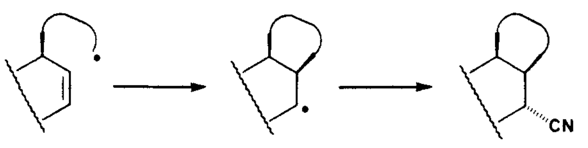
The successful transfer of a cyano group to the radical formed by a cyclization reaction (**1** → **2** → **3**)[1] owes its importance, inter alia, to the fact that together with the bromo acetal cyclization or its variants,[2] it becomes an important component of a method for positioning substituents on adjacent ring carbons with complete regiochemical and high stereochemical control (vide infra).

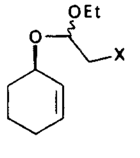


1 2 3

One of the requirements for successful trapping is minimization of hydrogen atom transfer to the cyclized radical **2**. This is particularly difficult when efficient hydrogen atom donors such as tin hydrides are used as a source of the tin radicals employed to generate the initial radical **1**.[3] Our original design of the cyano-trapping method,[1] therefore, avoided tin hydrides in favor of hexaphenyldistannane photolysis to produce the requisite tin radicals. This was successful in demonstrating the feasibility of the cyclization-trapping scheme, but it had several drawbacks, such as the formation of UV absorbing, insoluble, polymeric tin species. We therefore turned again to the possibility of using tin hydrides as a source of tin radicals.

We now report that we have succeeded in defining conditions that make practical the cyclization-cyano-trapping reaction, as well as other cyclization-trapping operations.

As we have reported previously,[1] even in the presence of an excess of *tert*-butyl isocyanide, the bromo acetal **4**, X = Br, cyclizes to **5** under otherwise typical cyclization conditions (0.1 M tributylstannane; AIBN; refluxing benzene) without yielding any appreciable amount of the cyano-trapping product **6**. It was, however, encouraging to find that very slow addition of tributylstannane did produce the desired cyano compound **6**, albeit in low yield.



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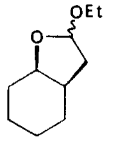

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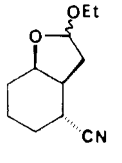

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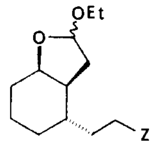

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Production of tin hydride in low concentration, as well as drastic reduction of the quantity of tin species required for the conversion of **4** to **6**, might be achieved by a sodium borohydride-catalytic tributyltin halide system.[4] We therefore noted with interest Giese's report that this system, using photolytic initiation in ethanol, was effective in adding radicals derived from alkyl iodides to electrophilic olefins.[5] Unfortunately, cyano-trapping failed under Giese's conditions, even with an excess of *tert*-butyl isocyanide. Only the simple cyclization product **5** could be obtained from **4**, X = Br or I.[6,7] In spite of this initial setback, success was eventually achieved by using *tert*-butanol as solvent and sodium cyanoborohydride as reducing agent.

The following experiment is typical: A mixture of 44 mg of iodo acetal **4**, X = I,[8,9] 19 mg (2 equiv) of sodium cyanoborohydride, 3 mg (0.1 equiv) of AIBN, 247 mg (20 equiv) of *tert*-butyl isocyanide, and 5 mg (0.1 equiv) of Bu_3SnCl in 4 mL of degassed *tert*-butyl alcohol was prepared and immediately refluxed for 4 h under argon.[10] Workup and purification[11] gave the

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(1) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6765.

(2) (a) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3720. (b) Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741. (c) Stork, G.; Kahn, M. *J. Am. Chem. Soc.* **1985**, *107*, 500. (d) Stork, G. "Selectivity—A Goal for Synthetic Efficiency"; Bartman, W., Trost, B. M., Ed.; Verlag Chemie: Basel, 1984; pp 281-299.

(3) For rates of reaction of carbon-centered radicals with tin hydrides, *tert*-butyl isocyanide, diethyl vinylphosphonate, and a variety of olefins, see respectively: Lusztyk, J.; Maillard, B.; Lindsay, D. A.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 3578. Blum, B. P.; Roberts, P. M. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1313. Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1981**, 161. Giese, B.; Meixner, J. *Chem. Ber.* **1981**, *114*, 2138.

(4) Cf.: Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1975**, *40*, 2554.

(5) Giese, B.; Gonzalez-Gomez, J. A.; Witzel, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 69.

(6) For simple radical cyclization, the catalytic tin process is obviously a convenient alternative to the use of stoichiometric tin hydrides.

(7) Significantly, the *tert*-butyl isocyanide was unaffected under these conditions.

(8) Iodo acetals are preferred because bromo acetals often lead to incomplete reaction in cyclization-trapping experiments using catalytic tin. Presumably, this reflects their difference in rates of reaction with tin radicals, which may also react with radical traps. Cf.: Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc* **1968**, *90*, 7047. Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343. Saegusa, T.; Kobayashi, S.; Ito, Y.; Yasuda, N. *J. Am. Chem. Soc.* **1968**, *90*, 4182.

(9) Mixed Iodo acetals are very easily prepared (>90% yield) by dropwise addition of a solution of ethyl vinyl ether (1.3 equiv) in methylene chloride to a stirred heterogeneous mixture of *N*-iodosuccinimide (1.05 equiv) and a primary or secondary alcohol in methylene chloride at -20 °C. Even the tertiary alcohol 1-vinylcyclohexanol gives 70% yield by this method. For a related procedure, see: Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564.

(10) The yield was the same on 10 times this scale. It is important to point out that *tert*-butyl alcohol and excess *tert*-butyl isocyanide can be distilled after completion of the reaction and reused without affecting the cyclization-trapping yields.

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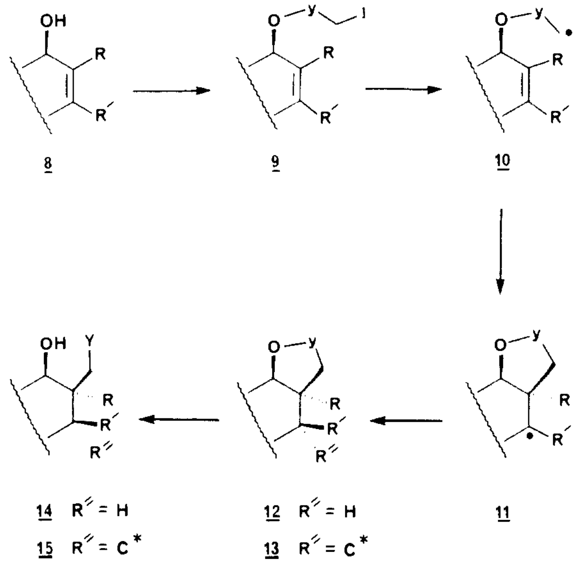
previously described cyano compound **6** in 60% yield.[12] An analogous procedure could be used with a variety of electrophilic olefin traps (10 equiv).[13] Acrylonitrile, methyl acrylate, ethyl vinyl ketone,[14] diethyl vinylphosphonate, methyl vinyl sulfone, and phenyl vinyl sulfone thus gave 55–75% yields of the trapped cyclized products **7**, Z = CN, CO_2Me, COEt, $PO(OEt)_2$, SO_2Me, and SO_2Ph, respectively.[15,16]

We conclude by noting that the cyclization–trapping process forms the final link in a general scheme which, starting with an allylic alcohol system (**8**), controls the structural problems attending formation of two adjacent chiral centers (**8** → **14** or **15** with y = temporary oxygen connection, Y = liberated functionality derived from y, e.g., y = CH(OEt), CMe(OMe),[17] or $SiMe_2$[2c] and Y = CHO, COMe, or OH, respectively). The control of regio- and stereochemistry derives from two factors: (1) The cyclization step (**10** → **11**) achieves regio- and stereospecific attachment of the operational equivalent of a functional carbon or a functional chain, CH_2Y, at the proximal end of the double bond and cis to the controlling allylic oxygen. (2) At the distal position, the cup shape of the cis-fused bicyclic radical intermediate **11** leads to trans delivery with respect to the controlling oxygen, either of a hydrogen (**11** → **12**) via simple radical cyclization or, as we report in this paper, of a functional carbon or a functional chain, C* (**11** → **13**).



The wealth of methods for establishing the required stereochemistry of the controlling hydroxyl, and the ease with which it could eventually be inverted or removed, should make this vicinal substitution scheme especially useful.

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

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[11] This consisted of addition of methylene chloride, vigorous shaking with 3% aqueous ammonia, addition of brine, separation of the organic phase, two further extractions with methylene chloride, drying, removal of methylene chloride and of *tert*-butyl alcohol (by azeotroping with benzene), and chromatography (silica; 10% ethyl acetate–petroleum ether).

[12] 8% of the easily separable epimeric cyano compound (and a small amount of **5**) was also formed in this reaction. Starting with the mixed iodo acetal from 2-cyclopentenol, the better defined cup shape of the bicyclic radical intermediate results in a 68% yield of the expected trans cyano product accompanied by only 2% of its epimer. Furthermore, trapping is equally successful at a tertiary radical center. Thus, the mixed iodo acetal of 3-methyl-2-cyclohexenol gives 62% of the expected trans cyano product and 5% of its epimer.

[13] In the case of electrophilic olefins, Giese's conditions[5] could be used, but the yields were at least as good, and in some cases much better, under our conditions. Under Giese's conditions, hydride reduction of the radical trap and conjugate addition of ethanol to the radical trap were problems observed in some cases.

[14] In this case, the solvent was THF, initiation was by photolysis (254 nm; quartz) at room temperature for 10 h, and 0.2 equiv of Bu_3SnCl was used.

[15] The products **7** were adequately characterized by spectral means after workup and purification as for **6**. Variable amounts of simple cyclization product **5** and of telomers were generally produced in addition of the desired products.

[16] It appears that electron-deficient olefins respond to stearic bias similarly to *tert*-butyl isocyanide. For instance, using acrylonitrile as the radical trap, 7, Z = CN, is produced in 70% yield accompanied by 8% of its epimer.

[17] A procedure similar to that of ref 9 appears satisfactory for the synthesis of mixed iodo ketals: from 2-cyanohexenol and 2-methoxypropene we obtained a >90% yield of mixed iodo ketal which was then successfully submitted to cyclization-trapping.

Deprotonation of Chelating Enamines. Direct Formation of β-Lithio Enamines

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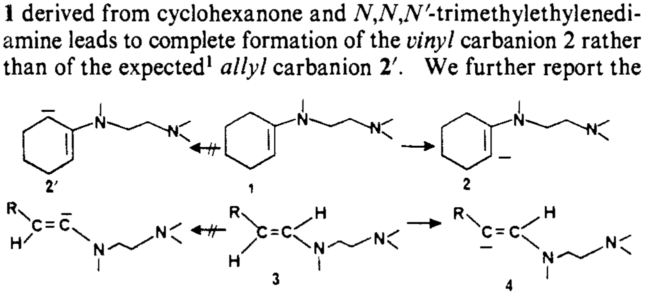
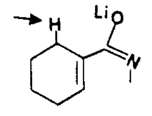
We report here that deprotonation of the chelating enamine **1** derived from cyclohexanone and *N,N,N'*-trimethylethylenediamine leads to complete formation of the *vinyl* carbanion 2 rather than of the expected[1] *allyl* carbanion **2'**. We further report the equally surprising result that chelating enamines (derived from aldehydes unbranched at the α-position) in which the competition now involves removal of either the α- or the *β-vinyl* hydrogen (**3**) lead to β-(**4**) rather than the expected α-deprotonation.[2]



These results are in striking contrast with the observations that chelation-mediated deprotonation of the related **5**[3] gives the anticipated allyl anion and that deprotonation of the simple vinylamine **6** (in the presence of tetramethylethylenediamine) takes place at the α position (arrows),[4] the normal result of deprotonation of heterosubstituted ethylenes.[5]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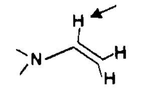
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[1] Morton, A. A.; Finnegan, R. A. *J. Polym. Sci.* **1959**, *38*, 19. Broaddus, C. D.; Much, D. L. *J. Am. Chem. Soc.* **1967**, *89*, 6533. Crawford, R. J.; Erman, W. F.; Broaddus, C. D. *J. Am. Chem. Soc.* **1972**, *94*, 4298. Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1976**, *59*, 453. The greater stability of the allylic vs. the vinyl carbanion is well established: See, inter alia: Dessy, R. E.; Kitching, W.; Psarras, T.; Salinger, R.; Chen, A.; Chivers, T. *J. Am. Chem. Soc.* **1966**, *88*, 460. Butin, K. P. Beletskaya, I. P.; Kashin, A. N.; Reutov, O. A. *J. Organomet. Chem.* **1967**, *10*, 197. Shatenshtein, A. I. *Adv. Phys. Org. Chem.* **1963**, *1*, 155.

[2] Varying amounts of β-deprotonation competition with α-deprotonation have been reported with enol ethers as early as 1952: Paul, R.; Tchelitcheff, S. Bull. Soc. Chim. Fr. **1952**, 208. See also: Soderquist, J. A.; Hsu, G. J. H. *Organometallics* **1982**, *1*, 830. Less obviously relevant cases include preferential β- vs. γ-deprotonation in certain vinyl ethers: McDougal, P. G.; Rico, J. R. *Tetrahedron Lett.* **1984**, *25*, 5977. For preferential α-deprotonation vs. allylic deprotonation in enol ethers, see: Rossi, A. R.; Reuillard, B. D.; Gould, S. J. *Tetrahedron Lett.* **1978**, 4357. For an interesting case involving vinyl vs. allyl deprotonation in an allyl alcohol system, see: Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315.

[3] Beak, P.; Kempf, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 4550.

[4] Bates, R. B.; Beavers, W. A.; Blacksberg, I. R. *Abstr. Pap.—Am. Chem. Soc.* **1975**, *169th*. See also: Schmidt, R. R.; Talbiersky, J.; Russeger, P. *Tetrahedron Lett.* **1979**, 4273 and papers cited therein.

[5] Special structural features can result in allylic γ-deprotonation of certain types of enamines related to **1** and to **3**: Ahlbrecht, H. *Chimia* **1977**, *31*, 391. Thompson, H. W.; Huegi, B. S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1603.

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