tional Cancer Institute, DHSS, and by a New York Sea Grant (J.C.).

Supplementary Material Available: Tables of fractional coordinates, interatomic distances, interatomic angles, and thermal parameters for nostocyclophane D (6 pages). Ordering information is given on any current masthead page.

Ligand Exchange between Cyanocuprates and Allylic Stannanes: A Novel, Direct Route to Allylic Cuprates Possessing Remarkable Reactivity and Stability

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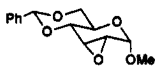
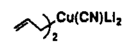
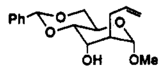
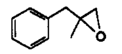
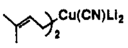
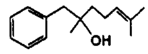
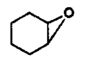
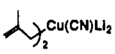
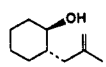
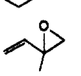
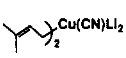
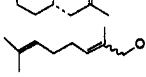
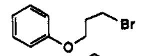
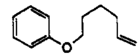
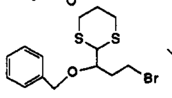
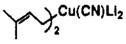
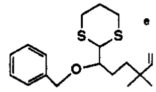
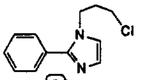
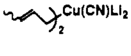
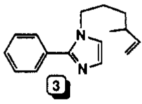
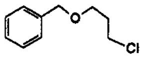
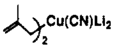
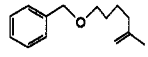
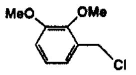
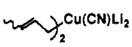
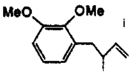
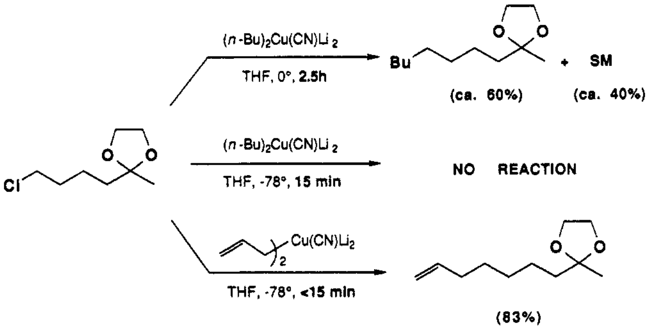
The lack of thermal stability associated with Gilman reagents (R_2CuLi) composed of allylic ligands, recently demonstrated in these laboratories,[2] can be used to rationalize the scarcity of successful organocopper reactions involving allylic cuprates in the past decade.[3] Indeed, even the preparation of dimeric $(allyl)_2CuLi$ at −78 °C affords significant percentages of Wurtz-like coupling material (1,5-hexadiene) together with aggregate $(allyl)_3Cu_2Li$,[2] which as a class of reagents is known to have considerably different chemical reactivities.[4] To circumvent these problems of reagent preparation and thermal instability, we now report a novel route to higher order (HO) allylic cyanocuprates based on direct transmetalations of precursor allylstannanes. The species so formed by this process (i.e., $R_2Cu(CN)Li_2$, R = an allylic group) are stable at 0 °C yet are extremely reactive toward substitution reactions (vide infra).[5]

Table I. Substitution Reactions of Allylic Cuprates Formed via Transmetalations of Allylic Stannanes with $Me_2Cu(CN)Li_2$ at 0 °C in THF for 30 min

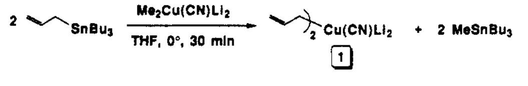
Entry	Educt	Reagent	Conditions	Product(s)^a	Yield(%)^b
1			0° to rt, 12h		98
2			-78°, 15 min		89
3			0°, 1 h		90
4			-78°, 15 min		74^c
5			-78°, 5 min		86
6			-78 to -40°, 2.5 h^d	 ^{e}	77(95)^f
7	 **2**		-78°, 1 h^d	 **3** ^{g}	84(0)^h
8			-78°, 15 min		88
9			-78°, 1 h	 ^{i}	84

^{a}Chromatographically pure; fully characterized by IR, NMR, MS, and HRMS data. ^{b}Isolated. ^{c}A 5:1 ratio of *E*:*Z* isomers. ^{d}Ten equivalents of Me_2S added. ^{e}Also contained 20% of the product of α-attack. ^{f}Based on recovered educt. ^{g}A 2:1 mix of γ:α (*Z* + *E*) isomers. ^{h}Yield obtained by using the corresponding LO crotylcuprate.[15] ^{i}A 9:1 mix of γ:α (*E*) isomers.

Scheme I



Treatment of allyltributylstannane with 0.5 equiv of the trivial, MeLi-derived cyanocuprate $Me_2Cu(CN)Li_2$[6] at 0 °C for 30 min affords cuprate **1** essentially quantitatively, as judged from ^1H NMR analysis (complete disappearance of the methyl signal at δ −1.50 ppm)[7] and assessment by quantitative VPC (measurement of $MeSnBu_3$ formed vs an internal standard). Similar conditions can be employed with other allylic stannanes, including those containing methallyl,[8] crotyl, and prenyl groups (eq 1).[9]

 (1)

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[1] Proctor & Gamble Predoctoral Fellow; awarded by the American Chemical Society, 1989–1990.

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[5] For some examples of substitution reactions involving allylic cuprates, see the following. (a) Lithium-based: Schauman, E.; Kirschning, A. *Tetrahedron Lett.* **1988**, *29*, 4281. Corriu, R. J. P.; Guerin, C.; M'Boula, J. *Ibid.* **1981**, *22*, 2985. Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1985**, *107*, 6137. (b) Grignard-based: Larcheveque, M.; Petit, Y. *Bull. Soc. Chim. Fr.* **1989**, 130. Beau, J.-M.; Aburaki, S.; Pougny, J.-R.; Sinay, P. *J. Am. Chem. Soc.* **1983**, *105*, 621. Cahiez, G.; Alexakis, A.; Normant, J. F. *Synthesis* **1978**, 528. Bourgain-Commercon, M.; Normant, J. F.; Villieras, J. *J. Chem. Res., Synop.* **1977**, 183. Fujisawa, T.; Sato, T.; Kawashima, M.; Nakagawa, M. *Chem. Lett.* **1981**, 1307. Sato, T.; Kawashima, M.; Fujisawa, T. *Ibid.* **1980**, 571. Kawashima, M.; Fujisawa, T. *Ibid.* **1984**, 1851. Sato, T.; Takeuchi, M.; Itoh, T.; Kawashima, M.; Fujisawa, T. *Tetrahedron Lett.* **1981**, *22*, 1817. Fujisawa, T.; Sato, T.; Kawara, T.; Kawashima, M.; Shimizu, H.; Ito, Y. *Ibid.* **1980**, *21*, 2181. Sato, T.; Kawashima, M.; Fujisawa, T. *Ibid.* **1981**, *22*, 2375. Fujisawa, T.; Sato, T.; Kawashima, M.; Naruse, K.; Tamai, K. *Ibid.* **1982**, *23*, 3583. Klein, J.; Levene, R. *Ibid.* **1974**, 2935. Normant, J. F.; Alexakis, A.; Cahiez, G. *Ibid.* **1980**, *21*, 935. Huynh, C.; Derguini-Boumechal, F.; Linstrumelle, G. *Ibid.* **1979**, 1503. Linstrumelle, G.; Lorne, R.; Dant, H. P. *Ibid.* **1978**, 4069. Derguini-Boumechal, F.; Lorne, R. Linstrumelle, G. *Ibid.* **1977**, 1181. Brockway, C.; Kocienski, P.; Pant, C. *J. Chem. Soc., Perkin Trans. 1* **1984**, 875. Drouin, J.; Leyendecker, F.; Conia, J. M. *Tetrahedron* **1980**, *36*, 1195. Courtois, G.; Harama, M.; Miginiac, L. *J. Organomet. Chem.* **1980**, *198*, 1.

[6] Lipshutz, B. H. *Synthesis* **1987**, 325. Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005.

[7] Lipshutz, B. H.; Kozlowski, J. A.; Wilhelm, R. S. *J. Org. Chem.* **1984**, *49*, 3943.

[8] VPC analysis of the transmetalation of methallyltributyltin indicated that this exchange went to the extent of ca. 85%. Due to the large difference in reactivities between the allylic cuprate and $Me_2Cu(CN)Li_2$, however, there was no competition by the alkylcuprate in subsequent alkylations (i.e., no methyl transfer under the conditions employed).

[9] The transmetalation process is sensitive to the quality and the manner in which the stannanes are stored. Hence, for maximum results, allylic tin reagents should be as pure as reasonably possible and stored in glass containers *without using rubber septa* (polyethylene stoppers are acceptable).

0002-7863/90/1512-4063$02.50/0

Although formed at 0 °C, HO allylic cuprates are best utilized at low temperatures with most sp^3-based electrophiles. Our data in Table I are highly suggestive of the variety of substrates that participate in these mild and efficient couplings.[10] Moreover, the following noteworthy features deserve special comment: (1) diprenylcyanocuprates, which react with epoxides by way of α-attack (entries 2 and 4), reverse this trend with halides where attachment at the γ-carbon prevails (entry 6); (2) crotylcuprates likewise react preferentially with halides at the γ-locale (entries 7 and 9); (3) cyclic epoxides (e.g., entry 3), highly prone toward Li^+-induced rearrangement to cyclic ketones,[11] undergo clean displacement with minimal Lewis acid related side-product formation; (4) the presence of heteroatoms, in particular sulfur (entry 6) and nitrogen (entry 7), which can oftentimes perturb cuprates by their copper and lithium ion sequestering properties, respectively, do not alter these reactivity patterns; (5) use of lower order, Gilman-like cuprates tend not to effect these displacements (see entry 7).

Perhaps most significant, in strong testimony to the intense reactivity of these allylic cuprates, is their ability to displace *primary, unactivated chlorides*. Normally, even with the most reactive of Gilman cuprates (i.e., those containing sp^3 carbon–copper bonds), chlorides are unacceptably slow at 0 °C[12] and are rarely used at room temperature[13] due to competing cuprate decomposition. Even higher order dialkylcyanocuprates normally require several hours at 0 °C to consume starting material.[12] By comparison, *allylic cuprates effect this transformation at −78 °C in minutes* (Scheme I).[14]

In summary, a new method for forming relatively thermally stable allylic cuprates has been discovered. These reagents appear to be among the most reactive cuprates presently known toward substitution processes. The preparation relies on ligand-exchange events[16] between alkyl cuprates and allylic stannanes, which completely eliminates the need for prior generation of allyllithium intermediates.

Acknowledgment. Financial support provided by the NSF (CHE 87-03757) and the donors of the Petroleum Research Fund (21791-AC1-C), administered by the American Chemical Society, is gratefully acknowledged.

Registry No. 1, 91328-60-8; **2**, 126036-05-3; **3**, 126035-99-2; (*E*)-$Me_2C{=}CH(CH_2)_2CH{=}C(Me)CH_2OH$, 32663-38-0; (*Z*)-$Me_2C{=}CH(CH_2)_2CH{=}C(Me)CH_2OH$, 58649-77-7; $PhO(CH_2)_4CH{=}CH_2$, 74972-56-8; $PhCH_2O(CH_2)_4C(Me){=}CH_2$, 126036-01-9; $PhO(CH_2)_3Br$, 588-63-6; $PhCH_2O(CH_2)_3Cl$, 26420-79-1; $(Me_2C{=}CHCH_2)_2Cu(CN)Li_2$, 122700-73-6; (*E*)-$Me(CH{=}CHCH_2)_2Cu(CN)Li_2$, 124020-72-0; (*Z*)-$(MeCH{=}CHCH_2)_2Cu(CN)Li_2$, 126036-06-4; $(H_2C{=}C(Me)CH_2)_2Cu(CN)Li_2$, 122700-72-5; $H_2C{=}CHCH_2SnBu_3$, 24850-33-7; $Me_2Cu(CN)Li_2$, 80473-70-7; $MeCH{=}CHCH_2Li$, 16327-44-9; methyl 4,6-O-benzylidene-2-deoxy-2-(2-propenyl)-α-D-allohexopyranoside, 126108-10-9; 2,6-dimethyl-1-phenyl-5-hepten-2-ol, 18091-00-4; *trans*-2-(2-methyl-1-propen-3-yl)-cyclohexan-1-ol, 101859-19-2; 6-(benzyloxy)-6-(1,3-dithian-2-yl)-3,3-dimethyl-1-hexene, 126035-97-0; 7-(benzyloxy)-7-(1,3-dithian-2-yl)-2-methyl-2-heptene, 126035-98-1; (*Z*)-7-(2-phenylimidazol-1-yl)-2-heptene, 126036-00-8; 4-(2,3-dimethoxyphenyl)-3-methyl-1-butene, 126036-02-0; (*Z*)-5-(2,3-dimethoxyphenyl)-2-pentene, 126036-03-1; 2-methoxy-6-phenyl-1a,2,3a,4-tetrahydrooxireno[4,5]pyrano[3,2-*d*][1,3]dioxin, 66537-92-6; 2-methyl-2-benzyloxirane, 36099-42-0; 7-oxabicyclo[4.1.0]heptane, 286-20-4; 2-ethenyl-2-methyloxirane, 1838-94-4; 3-(benzyloxy)-3-(1,3-dithian-2-yl)-1-bromopropane, 126036-04-2; 2,3-dimethoxy-1-(chloromethyl)benzene, 3893-01-4; 2-(4-chlorobutyl)-2-methyl-1,3-dioxolane, 57558-50-6; 2-methyl-2-(1-hepten-7-yl)-1,3-dioxolane, 76731-09-4.

Supplementary Material Available: A detailed, typical procedure and data (chromatographic, spectral, analytical) for all new compounds (3 pages). Ordering information is given on any current masthead page.

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[10] Displacements also occur in far simpler non-heteroatom-containing systems as well; e.g., *n*-heptyl bromide reacts with diallylcyanocuprate (−115 → −78 °C, 1 h) to afford decene in 90% (VPC) yield. Substitution reactions at sp^2 centers have also been studied in detail: Lipshutz, B. H.; Elworthy, T. R. *J. Org. Chem.*, in press.

[11] In the specific case of cyclohexene oxide, ca. 30% of the product mix consists of cyclohexanone; cf.: Lipshutz, B. H.; Kozlowski, J. A.; Parker, D. A.; Nguyen, S. L.; McCarthy, K. E. *J. Organomet. Chem.* **1985**, *285*, 437. See also: Bertz, S. H.; Dabbagh, G. *J. Org. Chem.* **1984**, *49*, 1119. Johnson, C. R.; Herr, R. W.; Wieland, D. M. *Ibid.* **1973**, *38*, 4263. Bertz, S. H.; Dabbagh, G. *J. Am. Chem. Soc.* **1982**, *104*, 5824. Acker, R.-D. *Tetrahedron Lett.* **1977**, 3407.

[12] Lipshutz, B. H.; Parker, D. A.; Kozlowski, J. A.; Miller, R. D. *J. Org. Chem.* **1983**, *48*, 3334.

[13] Whitesides, G. M.; Fischer, W. F.; San Filippo, J.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871.

[14] For comparison purposes, imidazole chloride **2** (see Table I, entry 7) was treated with crotyllithium (−78 °C, 20 min) to afford a 50% yield of **3** (no educt remained), while treatment of **2** with crotyl Grignard (−78 → 0 °C) returned 66% of the educt with none of **3** being formed.

[15] Only starting material was recovered (70.4%); base-line material was also formed.

[16] For a related transmetalation/conjugate addition study on vinylstannanes, see: Behling, J. R.; Babiak, K. A.; Ng, J. S.; Campbell, A. L.; Moretti, R.; Koerner, M.; Lipshutz, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 2641.

Structure of the 2-Butyl Cation. H-Bridged or Methyl Bridged?

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The nature of the 2-butyl cation has been the subject of many experimental and theoretical investigations and affords a continuing challenge for the structural chemist. This is the smallest secondary carbocation that can be stabilized by either C–C or C–H hyperconjugation.

The 2-butyl cation was first observed in superacid solution at −110 °C.[1] The ^1H NMR spectrum at −140 °C revealed only two peaks due to the very rapid 2,3-hydride shifts. The barrier must lie below 2.4 kcal/mol.[2] This rearrangement could not be frozen out even on the ^{13}C NMR time scale in the solid state at −190 °C.[3] Since the rate of such chemical exchange processes is often reduced in the solid state, this hydride-shift barrier in solution might be considerably less than 2.4 kcal/mol.[3] The fully ^1H coupled ^{13}C NMR spectrum shows a coupling pattern that agrees with a rapidly exchanging cation, where each central carbon is coupled simultaneously (on the NMR time scale) to the three central hydrogens.[4] By analyzing the isotope effects and their temperature dependence on both the ^1H and ^{13}C NMR spectra, Saunders and Walker concluded that the best fit was obtained with a model assuming two structures to be present.[5] It was

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[1] Saunders, M.; Hagen, E. L.; Rosenfeld, J. *J. Am. Chem. Soc.* **1968**, *90*, 6882–6884.

[2] Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 7082–7083.

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[4] Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5026–5039.

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