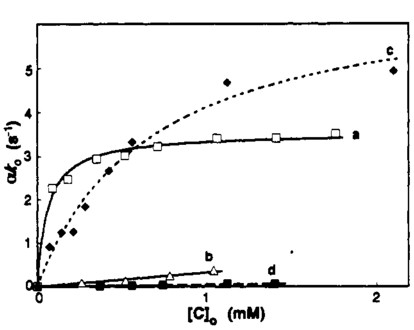
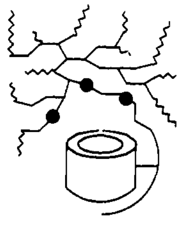


Figure 1. Plot of the pseudo-first-order rate constant against $[C]_0$ for deacylation of **2** (α = 1000) by CD–PEI (a) or PEI (b) and of **3** (α = 100) by CD–PEI (c) or PEI (d). Different α values were used for **2** and **3** in order to put their kinetic data on the same graphical scale. $[C]_0$ represents the total concentration of CD moiety of CD–PEI or CD. $[C]_0$ for PEI is taken as 1.4% of the residue molar concentration of PEI, so that it corresponds to the concentration of PEI moiety of CD–PEI. For b and d, k_0 is proportional to $[C]_0$. When $[C]_0$ = 0.3 mM, deacylation of **2** by CD–PEI was 30 or 600 times faster than that by PEI or CD, respectively. When $[C]_0$ = 0.6 mM, deacylation of **3** by CD–PEI was 160 or 900 times faster than that by PEI or CD, respectively.

atoms of PEI. Although several PEI derivatives manifest catalytic activity in various organic reactions, creation of specific binding sites on PEI is needed in order to mimic enzymes better. Many derivatives of CD have been prepared as enzyme mimics. Since CD is much smaller than enzymes, introduction of several catalytic groups on CD in positions suitable for high catalytic efficiency is not easy. Combination of PEI with CD may lead to a cavity-containing molecular skeleton suitable for incorporation of multiple catalytic elements. This is schematically illustrated in **1** where filled circles indicate possible catalytic functional groups.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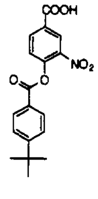

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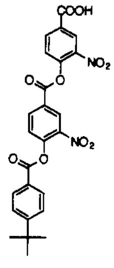

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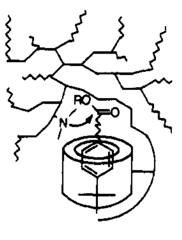

4

In the present study, β-CD was covalently linked to PEI by the reaction of PEI (0.55 monomeric residue mol) with mono-6-(p-tolylsulfonyl)-β-CD (7.7 mmol) in 200 mL of DMSO at 60 °C for 6 h followed by purification through dialysis, leading to a β-CD-containing PEI (CD–PEI). The content of CD in CD–PEI was estimated as 1.3% of the monomeric residues of PEI on the basis of initial burst kinetic studies (see below) and as 1.6% on the basis of elemental analysis. On the average, a PEI (MW 60 000) molecule contains 1400 monomeric residues, and therefore, CD–PEI contains 18–22 CDs.

Kinetics of the deacylation of esters **2** and **3** was studied in the presence of CD, PEI, or CD–PEI with $[C]_0 > [S]_0$ ($[C]_0$ is the initially added concentration of hosts and $[S]_0$ that of **2** or **3**; $[S]_0$ was ca. 5×10^{-5} M). Rate measurements were performed at pH 7.65 (0.5 M NaCl and 0.02 M phosphate buffer) and 25 °C in the presence of 1% (v/v) acetonitrile (used as the solvent for the stock solutions of **2** and **3**). Kinetic data are illustrated in Figure 1. Analysis of the saturation kinetic data of CD–PEI led to k_{cat} = $(3.53 \pm 0.08) \times 10^{-3}$ s^{-1} and K_m = $(6.00 \pm 0.88) \times 10^{-5}$ M for **2** and k_{cat} = $(6.81 \pm 0.58) \times 10^{-2}$ s^{-1} and K_m = $(6.52 \pm 1.24) \times 10^{-4}$ M for **3**. It appears that **2** is bound by CD–PEI more strongly than **3** and the carboxylate of **2** provides an extra binding interaction with the ammonium ion of CD–PEI.

The kinetics of deacylation of **2** or **3** was also examined in the presence of CD–PEI with $[C]_0 < [S]_0$. Biphasic kinetics was observed, and the amount of the phenol released during the initial burst stage corresponded to the amount of CD, indicating that acylation of the nucleophilic amine by the substrate inactivates CD–PEI. It is possible that the *tert*-butylbenzoyl group of the acylated polymer occupies the CD cavity.[7]

The efficient binding of **2** and **3** by CD–PEI, in contrast to the weak binding by PEI as reflected by the linear rate data of Figure 1, is achieved by the interaction of the *tert*-butylphenyl ring of the substrate with the CD ring. The greater reactivity of CD–PEI compared with PEI is due to efficient complexation of the esters by CD–PEI and effective nucleophilic attack within the complexes. The much faster rate of CD–PEI compared with CD indicates that the amino groups present on the PEI portion, instead of the hydroxyl group on the CD rim, act as the nucleophile (**4**). The amino groups on the PEI backbone may have better access to the ester linkage of the bound substrate.[8,9]

CD–PEI may be regarded as either a derivative of CD with a convergent nucleophile located above the CD cavity or a PEI derivative containing specific binding sites. The next step toward obtaining better artificial enzymes containing both PEI and CD is to introduce a second catalytic functional group in a planned position near the CD cavity.

Acknowledgment. This work was supported by the Organic Chemistry Research Center and the SNU Daewoo Research Fund.

Registry No. Mono-6-(p-tolylsulfonyl)-β-CD, 67217-55-4.

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(7) HPLC analysis of reaction products indicated that only 1 equiv of 4-carboxy-2-nitrophenol and no *tert*-butylbenzoate is released after deacylation of both **2** and **3** by CD–PEI.

(8) The k_{cat} value for CD-PEI-promoted deacylation of **3** is 19 times greater than that of **2**, whereas **3** is more reactive toward PEI than is **2** by only 40%. It is not clear which of the two ester groups of **3** is initially attacked by the amine of CD–PEI, although the greater k_{cat} for **3** compared with **2** indicates more effective attack at **3**.

(9) The average pK_a of the primary amine of PEI was reported to be 9.5, which is considerably smaller than that (10.6) of methylamine.[10] This may be attributed to the unfavorable electrostatic interactions among ammonium cations of the polymer, resulting in suppression of additional protonation. The electrostatic effect becomes more significant as more amines of PEI are protonated at lower pHs. For example, the amount of unprotonated amine was reduced by only 2 times when the pH was lowered from 8.5 to 7.5 in the case of PEI derivatives containing macrocyclic metal centers.[2] The fraction of the neutral amine at the pH (7.65) of the kinetic measurements, therefore, would be considerably greater than 1.4%, which is the value expected for a simple amine with the same pK_a value.

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Purification of Gram Quantities of C_{60}. A New Inexpensive and Facile Method

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Buckminsterfullerene (C_{60}), the newly discovered spherical allotrope of carbon, has precipitated a flurry of recent research endeavors.[1] A severe limitation to this research is the difficulty in producing gram quantities of C_{60} free of the higher molecular

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(1) (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. (b) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (c) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, *20*, 1423. (d) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630. (e) Diederich, F.; Whetten, R. L.; Thilgen, C.; Ettl, R.; Chao, I.; Alvarez, M. M. *Science* **1991**, *254*, 1768. (f) Whetten, R. L.; Alvarez, M. M.; Ans, S. J.; Schriver, K. E.; Beck, R. D.; Diederich, F. N.; Rubin, Y.; Ettl, R.; Foote, C. S.; Darmanyan, A. P.; Arbogast, J. W. *Mater. Res. Soc. Symp. Proc.* **1991**, *206*, 639. (g) For a recent review on fullerenes, see: McLafferty, F. W., Ed. *Acc. Chem. Res.* **1992**, *25*, 97.

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weight fullerenes. We describe here a simple and low-cost method that uses common laboratory glassware and reagents for the purification of even gram quantities of C_{60} in less than 1.5 h using activated charcoal as a stationary phase in a flash chromatography column.

Crude fullerene extracts from carbon arc soot contain 70–85% C_{60} and 10–15% C_{70} with the remainder being higher fullerenes.[1] The most common method for purifying crude C_{60} is column chromatography on activity grade I neutral alumina.[2] Our experience with this method has shown that to obtain 1 g of pure C_{60} requires 10 kg of alumina and 50 L of solvent, and the procedure takes 16–20 h. About 50% C_{60} of a possible 75% C_{60} present in the crude can be recovered since activity grade I alumina irreversibly adsorbs some of the C_{60}.[2] Alumina columns within modified Soxhlet extractors can be used to significantly simplify this method, but recovery yields are generally in the range of 33–43% out of a possible 75% C_{60} present.[3] Powdered graphite has been used as the stationary phase for chromatographic purification of C_{60}, but the recovery of C_{60} is only 32% of a possible 75%.[4] HPLC has been used for C_{60} purification, but it is primarily useful only for small-scale separations.[5,6]

A typical gram-quantity C_{60} purification procedure using our newly developed methods is as follows. A slurry of alkaline decolorizing carbon Norit-A[7] (36 g) and silica gel[8] (72 g) in toluene[9] (200 mL) was poured into a typical glass flash chromatography column (38-mm-diameter column, 45 cm long) that had a cotton plug at the bottom of the column.[10] The slurry was allowed to settle as the solvent *above* the stationary phase was allowed to drain under a head pressure of 7.5 psi of N_2 applied at the top of the column.[11] The stationary phase must not be allowed to become solvent free or else cracking of the stationary phase can occur. A homogeneous saturated toluene (400 mL) solution of 1.85 g of crude fullerenes (sonication of the mixture was used to facilitate the dissolution process) extracted from carbon arc soot was slowly poured onto the top of the Norit-A/silica gel stationary phase.[12] A head pressure of 7.5 psi of N_2 was applied, thus providing a ~16 mL/min elution rate.[13] The deep purple-colored solution containing C_{60} started to elute from the column after 37 min. After 36 min more, the eluant was nearly colorless, and collection of a second fraction was then begun. The total volume of toluene needed for obtaining the C_{60} fraction (first fraction) was ~600 mL. After 3 min more, a red-brown band characteristic of C_{70} started to elute. Removal of the solvent from the purple fraction afforded 1.16 g of C_{60} (63% of a possible 75% C_{60} in extractable fullerenes). ^{13}C NMR (125 MHz, C_6H_6) analysis of the C_{60} showed only one peak at δ 143.29 ppm, with no other peaks in the spectrum, while the signal to noise ratio was 68:1.[14] Likewise, mass spectrometric (MS) analysis showed a peak at 720 amu, with no detectable peaks for higher molecular weight fullerenes.[15] HPLC on silica gel showed only C_{60} in the first fraction with no detection of other fullerenes.[16] While the second band eluted from the column was red-brown, it did contain some C_{60}. One more, smaller chromatographic run on the initial red-brown portion afforded 74 mg more of C_{60} and 120 mg of a sample that was 1:5 in C_{60}:C_{70} as judged by peak height comparison of the MS signals[15] and 1:10 in C_{60}:C_{70} as judged by HPLC analysis.[16,17]

Although we illustrated this procedure with 1.85 g of extractable fullerenes, it worked equally well on a smaller scale using proportionately smaller stationary phases and solvent volumes. Norit-A alone as the stationary phase without silica gel as a cophase worked excellently for C_{60} separations on smaller scales (i.e., 100 mg of crude fullerenes with 2.0 g of Norit-A); however, the silica gel prevents cracking of the stationary phase in the larger columns and allows for higher flow rates. We also verified the reproducibility of the C_{60} separations by using Norit-A from a different distributor (Matheson Coleman & Bell), and the results were nearly identical. Norit-A/Celite-521 as a stationary phase

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(7) (a) Alkaline decolorizing carbon Norit-A was purchased from Fisher Scientific Company. (b) Activated carbon has been used extensively as a stationary phase for molecular size selection-based chromatography, and it was this feature that promoted our initial investigation. See: Gordon, A. J.; Ford, R. A. *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*; Wiley: New York, 1972; p 373.

(8) (a) Flash chromatography grade silica gel 60 (230–400 mesh ASTM, 0.040–0.063-mm particle size) was purchased from EM science. (b) For the use of silica gel as a co-stationary phase with activated charcoal for the separation of PCBs, see: Sericano, J. L.; El-Husseini, A. M.; Wade, T. L. *Chemosphere* **1991**, *23*, 915. We thank Professor T. Bidleman for providing us with this reference. (c) Silica gel alone is not sufficient for the separation of fullerenes; see: Heath, J. R.; Hawkins, J. M.; Alivasatos, P. A.; Sakally, R. J.; Lewis, T. A.; Loren, S. D.; Meyer, A.; Shibato, Y.; Tolbert, S.; Shang, *J. Mater. Res. Soc. Symp. Proc.* **1991**, *206*, 667.

(9) ACS grade toluene was purchased from EM Science.

(10) (a) The design of a typical flash chromatography column can be found in the following: Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923. (b) After calculating the appropriate amount of stationary phase necessary, use a column such that the stationary phase is ~10 times longer than the column diameter.

(11) **CAUTION**: Though we experienced no rupture of the standard glass columns under 7.5–10-psi pressures, we recommend utilization of this procedure behind a protective transparent shield to prevent injury if a rupture should occur. Additionally, thick-walled flash chromatography columns that are tape-wrapped would provide added protection.

(12) The Norit-A tends to irreversibly adsorb some of the fullerenes, with C_{70} adsorbed in preference to the C_{60}. When using the amount of Norit-A per gram of crude fullerenes described here, the amount of C_{60} irreversibly adsorbed is minimal. However, if more Norit-A per gram of crude fullerenes is used, some of the desired C_{60} will be irreversibly adsorbed. Thus an accurate determination of the amount of crude fullerenes is necessary, and the method of soot treatment prior to chromatography is important. We treat our plasma arc generated soot as follows. Toluene (500 mL) was added to carbon arc soot (14 g), and the mixture was placed in a sonicator bath for 30 min. The black soot suspension was then filtered through a pad of Celite-521 in a fritted-glass funnel to give a dark red-brown solution. The solvent was removed by rotary evaporation to give a black powder that was suspended in ether, and the suspension was poured onto the top of a 4-inch plug of silica gel. While at the top of the plug, the crude material was washed generously with ether. The discarded ether washings removed the grease residues and various hydrocarbon side products of the fullerene preparation. The fullerenes were then flushed through the column with distilled toluene, and the solvent was removed to afford 1.85 g of soluble fullerenes. Neglect of this type of treatment will undoubtedly cause hydrocarbon and insoluble particulates to inaccurately enhance the reported crude fullerene yields. Then determine, on the basis of the amount of crude fullerenes thus obtained, the relative amount of Norit-A, silica gel, and toluene necessary. One can only bypass the two-step crude fullerene preparation if one is confident of the amount of actual crude fullerenes (not crude fullerenes plus other organics plus insoluble particulate) in the mixtures.

(13) (a) The flow rate will vary depending on the size of the column. We have found that maintaining a head presssure of 7.5–10 psi will provide an excellent separation. (b) The stopcock at the bottom of the column can be closed and the pressure slowly released so that more toluene, as needed, can be added. See ref 10.

(14) The parameters used for the ^{13}C NMR analysis were optimized to readily show both C_{60} and C_{70}. A spectrum of the initial crude mixture using the same scanning parameters showed the C_{60} resonance at δ 143.29 (100) ppm and the C_{70} resonances at δ 150.73 (4), 148.18 (11), 147.48 (5), 145.44 (9), and 130.94 (3) ppm. The numbers in parentheses are the relative peak heights.

(15) The mass spectrum was recorded up to 1200 amu. The crude material showed C_{60} at 720 amu and C_{70} at 840 amu in a peak height ratio of 10:0.8.

(16) HPLC was carried out on an Alltech Econosphere silica gel column (250 mm × 4.6 mm i.d.) with 2% toluene in hexane at 1 mL/min using UV detection at 284 nm. The crude material showed a mixture of C_{60}, C_{70}, C_{84}, and possibly other higher fullerenes in a peak area ratio of 58.0:38.9:1.6:1.5, respectively. The retention times were 5.1, 5.9, 6.6, and 7.4 min, respectively, with base-line separation. Thus, at 284 nm, the extinction coefficient of C_{70} appears to be greater than that of C_{60}, therefore skewing detection in favor of C_{70}.

(17) Thus the combined yield of purified C_{60} after two columns was 67% of a possible 75% C_{60} in extractable fullerenes.

is inferior to the Norit-A/silica gel because, with the former, packing is more difficult and cracking of the stationary phase occurs easily. Molecular sieves (13X pellets ground to a fine powder and packed in a column) were used as a stationary phase and proved to be inadequate for C_{60} purifications.

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Preparation and Use of Vinylic *Lithio*cyanocuprates Containing an ω-Electrophilic Center

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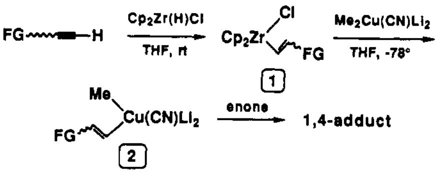
Traditional cuprate formation, as originally prescribed by Gilman,[1] bears a fundamental limitation in its reliance on organolithium precursors (i.e., 2RLi + CuX). Thus, lithiocuprates of either the lower order (LO, R_2CuLi) or higher order (HO, $R_2Cu(CN)Li_2$) persuasion which contain electrophilic centers (e.g., an ester or nitrile group) in R are presently unknown.[2] To circumvent the incompatibility of a highly reactive organolithium containing such a useful functionality, more stable organometallics have been developed, most notably from the Knochel,[3] Rieke,[4] and Piers[2] groups. However, the price paid for switching from lithium to other gegenions[3] is the lowering of cuprate reactivity, a general observation characteristic of both neutral species (i.e., "RCu·LiX")[5] as well as *ate* complexes (R_2CuM[6a]/$R_2Cu(CN)MM'$[6b]). In this report, we now describe the first method for generation of vinylic lithiocuprates which contain internal electrophiles utilizing a transmetalation strategy based on readily available zirconium intermediates **1**[7] (Scheme I).

Scheme I



Scheme II

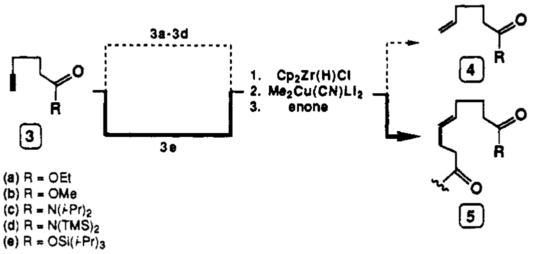


Table I. Formation and Reactions of Functionalized Lithiocuprates

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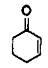
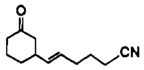
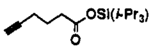
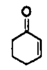
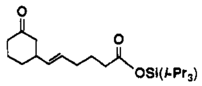
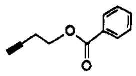
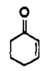
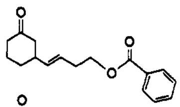
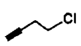
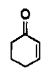
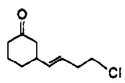
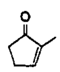
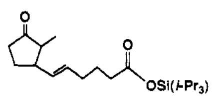
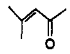
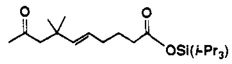
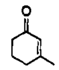
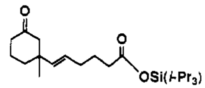
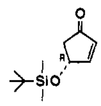
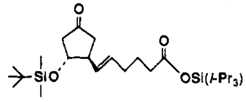
1				75
2	 **3e**			75
3				71[c]
4				93[c]
5	**3e**			83[c,d]
6	**3e**			82[c]
7	**3e**			71[c,e]
8	**3e**			76[c,d]

[a] Fully characterized by IR, NMR, MS, and HRMS data. [b] Isolated yields. [c] $BF_3 \cdot Et_2O$ (1 equiv) was added to the cuprate prior to introduction of the enone. [d] One isomer by capillary GC. [e] Yield was 35% without $BF_3 \cdot Et_2O$.

Treatment of a vinylzirconate **1**, easily prepared from 1-alkynes using $Cp_2Zr(H)Cl$ in THF (room temperature, 15 min),[8] with the trivial HO cuprate $Me_2Cu(CN)Li_2$ at low temperatures (−78 °C, 15 min) leads directly to the mixed cuprate **2**. Introduction of an α,β-unsaturated ketone, neat or in THF, to the newly generated cuprate at this temperature affords the expected 1,4-adduct in good isolated yields. This simple, one-pot process can be applied to acetylenes which possess a nitrile, ester, or chloride residue (Table I). It is especially noteworthy that β,β-disubstituted enones react readily at −78 °C, a clearly distinguishable feature between these lithiocuprates and, for example, zinc halide-containing reagents.[9] Moreover, the rapidity and simplicity associated with this hydrozirconation–transmetalation–Michael addition sequence are also attractive elements, as there is no major time commitment to prior generation of activated organometallics (i.e., $RZnX^2$ or $Cu(0)^3$).

An unexpected observation was made in the case of 5-hexynoic acid ethyl or methyl ester (**3a,b**), where the sequence described

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(1) Gilman, H.; Jones, R. G.; Woods, L. A. *J. Org. Chem.* **1952**, *17*, 1630.

(2) There is an example of an LO lithiocuprate containing a primary chloride, see: Piers, E.; Roberge, J. Y. *Tetrahedron Lett.* **1991**, *32*, 5219. Piers, E.; Yeung, B. W. A. *J. Org. Chem.* **1984**, *49*, 4567. Piers, E.; Karunaratne, V. *J. Chem. Soc., Chem. Commun.* **1983**, 935.

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(5) Neutral complexes of this type are normally relatively unreactive[5b] unless used in the presence of, for example, a Lewis acid, see: Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 947. (b) Lipshutz, B. H.; Sengupta, S. *Org. React.*, in press. Posner, G. H. *Ibid.* **1975**, *22*, 253; *Ibid.* **1972**, *19*, 1.

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