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900 (m), 887 (w), 829 (w), 805 br (w), 739 (w), 650 (w); UV λ_{max} (EtOH) 209.3, 240.9, 249.9, 276.9, 286.1, 330.3, 361.3.

3: mp 164.7–165.2 °C; ^{1}H NMR (Table I); MS *m/z* 502 (M$^+$), 459 (M – *i*-Pr)$^+$; IR (KBr) 2980 (s), 2929 (m), 2872 (m), 1610 (w), 1568 (w), 1530 br (s), 1462 (m), 1387 (m), 1369 (s), 1335 (w), 1290 (w), 1275 (w), 1260 (w), 1050 (m), 979 (w), 898 (w), 817 (w), 779 (w), 762 (w), 660 (w); UV λ_{max} (EtOH) 205.3, 252.9, 289.7, 360.9.

11: mp 172.1–172.9 °C; ^{1}H NMR (Table I); MS *m/z* 415 (M$^+$), 398; UV λ_{max} (EtOH) 205.3, 246.1, 273.5, 284.9, 345.7, 405.9.

26 (air-sensitive yellow substance): ^{1}H NMR (250 MHz, $CDCl_3$) 8.07 (2 H, s), 7.60 (2 H, s), 7.56 (1 H, s), 7.35 (1 H, d, *J* = 3.14 Hz), 6.50 (1 H, d, *J* = 3.14 Hz), 1.92 (3 H, s), 4.05, 3.95, 3.25 [m, *i*-Pr (CH)] 1.55–1.27 [d, *i*-Pr (Me)].

Aprotic Nitration. (a) In $CHCl_3$. In a typical experiment, a slurry of the nitronium salt (usually 2.2 molar equiv) in dry $CHCl_3$ was added to a solution of the isopropylpyrene substrate (0.15–0.20 mmol) in ca. 8 mL of $CHCl_3$ with vigorous mixing inside a drybox. After 30–45 min at room temperature the reaction mixture was removed from of the drybox, quenched with ice-bicarbonate, extracted (CH_2Cl_2), dried ($MgSO_4$), and separated. Solvent was removed and the residue was taken up in $CDCl_3$ for NMR analysis. In experiments in which the reaction mixture was examined directly by NMR prior to workup, $CDCl_3$ was used as solvent and an aliquot was directly withdrawn and transferred into a 5-mm NMR tube.

(b) In CH_3CN. The procedure was similar except that a homogeneous solution of the nitronium salt was prepared in dry acetonitrile inside the drybox (vortex) and slowly injected via a syringe into a solution of the isopropylpyrene in acetonitrile with vigorous mixing. CD_3CN was used as solvent in reactions which were examined by NMR prior to workup.

Reaction of 1 with $NO_2^+BF_4^-$ in CD_3CN. (a) $NO_2^+BF_4^-$ (0.113 g, 0.85 mmol; 2.2 equiv) was charged into a dry 5-mm NMR tube inside the glovebox. CD_3CN (0.5 mL) was added via a pipet and the mixture was vigorously mixed (vortex) until homogeneous. The content of the NMR tube was slowly poured into a solution of **1** (0.165 g, 0.4 mmol) in CD_3CN (0.5 mL) prepared in a 10-mm NMR tube under dry nitrogen at dry ice/acetone temperature with vigorous mixing (vortex), whereupon a dark red homogeneous solution was immediately formed. It was allowed to reach room temperature while mixing. After 10 min, an aliquot was transferred via a pipet into a 5-mm NMR tube and examined directly by ^{1}H NMR, prior to workup.

(b) Alternatively, the general procedure outlined for aprotic nitration in acetonitrile was adopted, with the initial reaction temperature of ca. –60 °C, followed by room temperature mixing.

Reaction of 1 with $NO_2^+BF_4^-$ and $NO^+BF_4^-$ in $CDCl_3$. $NO_2^+BF_4^-$ (12 mg, 0.09 mmol; 2 equiv) was charged into a dry 5-mm NMR tube under a dry nitrogen atmosphere and diluted with 5 drops of $CDCl_3$. The tube was cooled in a dry ice/acetone bath and a solution of **1** (18 mg, 0.045 mmol) in 0.4 mL of $CDCl_3$ was slowly added. The temperature was allowed to rise slowly to rt to give a deep red brown solution which was directly examined by NMR. Following 24 h at –70 °C, the same sample was studied by ESR at 240 K.

Following the same procedure, to $NO^+BF_4^-$ (19 mg; 0.16 mmol; 4 equiv) slurried in $CDCl_3$ (ca. 10 drops) was added **1** (16 mg, 0.04 mmol) at low temperature. Following vortex mixing and a raise in temperature, a persistent red brown solution was obtained which was studied by ^{1}H NMR and ESR.

Protonation of Nitropyrenes. Typically, to 20 mg of the nitropyrene substrate suspended or dissolved in ca. 0.5 mL of SO_2 was added a clear solution of the superacid (1 mL) diluted in ca. 1 mL of SO_2 at dry ice/acetone temperature with efficient vortex mixing. The resulting dark red (**2** and **3**), dark blue (1-nitropyrene), or green brown (2-nitropyrene) solution was transferred into a pre-cooled NMR tube under nitrogen with CD_2Cl_2 as internal lock and reference. The cold NMR tube was quickly inserted into the pre-cooled NMR probe at –70 °C; the sample was spun for ca. 5 min prior to data collection.

Transfer–Nitration. The cold ion solution, generated as indicated above, was carefully added to a cold solution of 5 mL of the aromatic (toluene, mesitylene, or benzene) diluted in 20 mL of dry CH_2Cl_2 at dry ice–acetone temperature with vigorous magnetic stirring; a dark green solution was formed. The cold bath was removed and the reaction mixture was allowed to reach room temperature. Stirring was continued for an additional 30 min, prior to workup and GC analysis.

Calculations. MMX force field energy calculations and structure minimizations were performed with a PCMODEL program (Serena Software). Good convergence was achieved usually after 100–150 iterations. All carbons of the pyrene skeleton were assigned π-atoms (SCF-π calculations were not available). The π-system in the minimized structures was planar. For the pyrenium ion of transfer–nitration, C_2 (ortho) was specified as C^+.

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Supplementary Material Available: ^{1}H NMR spectra of **2** and its protonation in TfOH/SO_2 at –65 °C and in TfOH at room temperature, **3** and its protonation in FSO_3H/SO_2, protonation of **24** and **25** in Magic acid/SO_2, and reaction of **1** with $NO_2^+BF_4^-$ and with $NO^+BF_4^-$ in acetonitrile and in chloroform, ESR spectra of reaction of **1** with $NO_2^+BF_4^-/CDCl_3$ and $NO^+BF_4^-/CDCl_3$, aprotic nitration of **10**, and UV spectra of **1**, **2**, and **11** (42 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Chemical Modification of Halogenated Polystyrene Resins Utilizing Highly Reactive Calcium and the Formation of Calcium Cuprate Reagents in the Preparation of Functionalized Polymers

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Polymeric organocalcium reagents have been prepared from highly reactive calcium and cross-linked polystyrene resins containing halogens (Br, Cl, F, CH_2Cl) and subsequent addition of electrophiles to yield functionalized polymers. Transmetalation with CuCN·2LiBr yields calcium cuprate reagents which react with a variety of electrophiles to prepare highly derivatized polymers.

The chemical modification of cross-linked polymers has received considerable interest since the discovery of Merrifield's resin and its use in peptide syntheses.[1] For almost 30 years, cross-linked polystyrene resins have been

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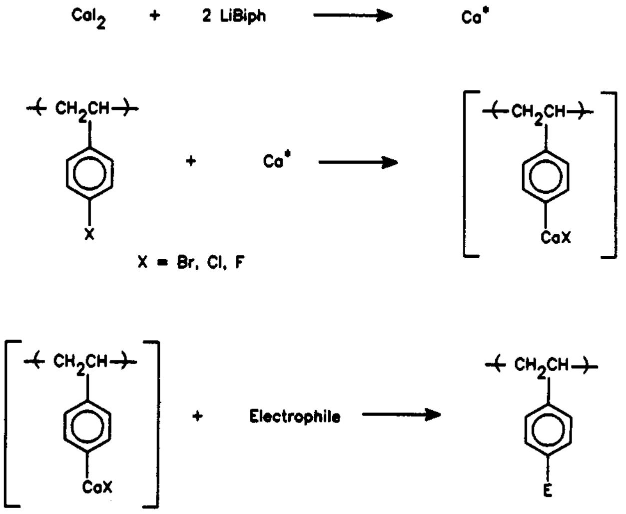
mainstays in solid-phase syntheses,[2] as reagents,[3] chiral auxiliaries in asymmetric syntheses,[4] or protecting groups in organic synthesis[5] as well as supports for chromatography[6] and catalysis.[7] Methods for functionalizing cross-linked polystyrene resins have been extensively published in the literature involving the lithiation of *p*-bromopolystyrene[8] and polystyrene[9] as well as nucleophilic substitution on chloromethylated polystyrene.[10] Brix and Clark have reported the preparation of the lithium and potassium derivatives of chloromethylated polystyrene under mild reaction conditions.[11] Several years ago, Fréchet et al.[12a,b] and Harvey and Raston[12c] reported the formation of insoluble Grignard reagents in THF from the addition of a soluble magnesium anthracene to lightly cross-linked polymers containing chloromethyl groups and alkyl and aryl bromides. We have previously reported that highly reactive calcium readily reacts with lightly cross-linked polystyrene resins containing chloromethyl, bromine, chlorine, and fluorine moieties to prepare functionalized polymers in excellent yields.[13,14] In this paper, we report additional results utilizing highly reactive calcium to prepare insoluble organocalcium reagents and subsequent transmetalation with CuCN·2LiBr to yield calcium cuprate reagents. These reagents, in turn, can be used to carry out a number of useful transformations on the polymer. Significantly, this approach can be used to introduce a second functional group into a polymer which contains a halogen as well as another functional group.

Table I. Reaction Conditions of Halogenated Polystyrene Resins with Highly Reactive Calcium

entry	starting polystyrene	time (h)	temp (°C)	loss of X^a
1	Ⓟ-Br^{b,c}	4	60	100
2	Ⓟ-Br^{b,c}	24	rt	79
3	Ⓟ-Br^{b,c}	36	rt	100
4	Ⓟ-Br^{b,e}	48	rt	86
5	Ⓟ-Br^{d,e}	72	rt	100
6	Ⓟ-$CH_2Cl^{d,f}$	6	0	100
7	Ⓟ-$CH_2Cl^{d,f}$	6	rt	100
8	Ⓟ-$CH_2Cl^{b,g}$	24	rt	77
9	Ⓟ-$CH_2Cl^{b,g}$	36	rt	100
10	Ⓟ-$CH_2Cl^{b,g}$	4	60	100
11	Ⓟ-Cl^{d,h}	80	rt^j	100
12	Ⓟ-F^{d,i}	80	rt^j	100

[a] Based on elemental analysis of polymer, X = halogen. [b] [Ca*]/[X] = 2.5:1. [c] *p*-Bromopolystyrene, 2.44 mmol of Br/g, DF = 0.31, 2% DVB. [d] [Ca*]/[X] = 1.5:1. [e] *p*-Bromopolystyrene, 5.47 mmol of Br/g, DF = 0.98, 2% DVB. [f] Chloromethylated polystyrene, 1.06 mmol of Cl/g, DF = 0.11, 1% DVB. [g] Chloromethylated polystyrene, 5.50 mmol of Cl/g, DF = 0.80, 2% DVB. [h] *p*-Chloropolystyrene, 3.75 mmol of Cl/g, DF = 0.45, 3% DVB. [i] *p*-Fluoropolystyrene, 2.59 mmol of F/g, DF = 0.28, 3% DVB. [j] Stirred at −78 °C for 1 h with warming to rt.

Scheme I



Preparation and Reaction of Organocalcium Reagents. The use of organocalcium reagents in organic chemistry has been slowed by the general unreactivity of standard forms of calcium toward oxidative addition reactions.[15] The preparation of an activated form of calcium was reported involving the reduction of calcium iodide with potassium metal in THF or toluene under nitrogen at ambient or reflux temperatures.[16] We recently reported the preparation of a soluble highly reactive form of calcium which undergoes rapid oxidative addition to a variety of carbon halogen bonds to generate the corresponding organocalcium reagents in excellent yields.[17] This success with organocalcium reagents suggested the possible extension to cross-linked polymers containing halogens.

Highly reactive calcium (Ca*) was prepared by the reduction of anhydrous calcium(II) iodide in a tetrahydrofuran solution with preformed lithium biphenylide under argon at room temperature. The reactivity of the highly

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(1) Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149.

(2) (a) Hodge, P., Sherrington, D. C., Eds. *Polymer-Supported Reactions in Organic Synthesis*; Wiley and Sons: New York, 1980. (b) Akelah, A., Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557.

(3) Leznoff, C. C. *Chem. Soc. Rev.* **1974**, *3*, 65.

(4) (a) Farrall, M. J.; Alexis, M.; Trecarten, M. *Nouv. J. Chim.* **1983**, *7*, 449. (b) Lecavalier, P.; Bald, E.; Jiang, Y.; Fréchet, J. M. J.; Hodge, P. *React. Polym.* **1985**, *3*, 315.

(5) (a) Fréchet, J. M. J. *Tetrahedron* **1981**, *37*, 663. (b) Patchornik, A.; Kraus, M. A. *J. Am. Chem. Soc.* **1970**, *92*, 7587.

(6) Neckers, D. C. *J. Chem. Educ.* **1975**, *52*, 695.

(7) (a) Pittman, C. U., Jr.; Evans, E. O. *Chem. Technol.* **1973**, 560. (b) Michalska, Z. M.; Webster, D. E. *Chem. Technol.* **1975**, 117. (c) Grubbs, R. H. *Chem. Technol.* **1977**, 512. (d) Lieto, J.; Milstein, D.; Albright, R. L.; Minkiewicz, J. V.; Gates, B. C. *Chem. Technol.* **1983**, 46. (e) Tsonis, C. P. *J. Chem. Ed.* **1984**, *61*, 479. (f) Pittman, C. U., Jr. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 8, Chapter 8, pp 553–611.

(8) (a) Camps, F.; Castells, J.; Fernando, M. J.; Font, J. *Tetrahedron Lett.* **1971**, 1713. (b) Farrall, M. J.; Fréchet, J. M. J. *J. Org. Chem.* **1976**, *41*, 3877 and references cited therein.

(9) (a) Braun, D. *Makromol. Chem.* **1959**, *30*, 85. (b) Chalk, A. J. *J. Polym. Sci. Part B* **1968**, *6*, 649. (c) Evans, D. C.; Phillips, L.; Barrie, J. A.; George, M. H. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 199.

(10) (a) Sherrington, D. C.; Hodge, P., Eds. *Synthesis and Separations using Functional Polymers*; Wiley and Sons: New York, 1988; pp 43–122 and references cited therein. (b) Mathur, N. K.; Narang, C. K.; Williams, R. E. *Polymers as Aids in Organic Chemistry*; Academic Press: New York, 1980.

(11) (a) Brix, B.; Clark, T. *J. Org. Chem.* **1988**, *53*, 3365. (b) Mix, H. *Z. Chem.* **1979**, *19*, 148.

(12) (a) Itsuno, S.; Darling, G. D.; Stöver, H. D. H.; Frécht, J. M. J. *J. Org. Chem.* **1987**, *52*, 4645 and references cited therein. (b) Itsuno, S.; Darling, G. D.; Lu, P. Z.; Fréchet, J. M. J. *J. Polym. Mater. Sci. Eng.* **1987**, *57*, 570. (c) Harvey, S.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1988**, *10*, 652 and references cited therein.

(13) A patent application covering the technology described herein has been filed by the authors of this paper.

(14) O'Brien, R. A.; Chen, T.; Rieke, R. D. *J. Inorg. Organomet. Polym.*, in press.

(15) (a) Hanusa, T. P. New Developments in the Organometallic Chemistry of Calcium, Strontium and Barium. *Polyhedron* **1990**, *9*, 1345. (b) Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Vol. 1, Chapter 4, pp 223–252. (c) Ioffe, S. T.; Nesmeyanov, A. *The Organic Compounds of Magnesium, Beryllium, Calcium, Strontium and Barium*: North Holland, Amsterdam, 1967.

(16) (a) McCormick, M. J.; Moon, K. B.; Jones, S. R.; Hanusa, T. P. *J. Chem. Soc., Chem. Commun.* **1990**, 778 and references cited therein. (b) The term "activated calcium" was earlier reported: Bryce-Smith, D.; Skinner, A. C. *J. Chem. Soc.* **1963**, 577.

(17) Wu, T.-C.; Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1990**, *55*, 5045.

Table II. Reactions Involving Organocalcium Reagents Prepared from *p*-Bromopolystyrene[a] and Highly Reactive Calcium

entry	electrophile	polystyrene product	yield[b] (%)
1	H_2O	Ⓟ-H	100
2	D_2O	Ⓟ-D[c]	
3	CO_2	Ⓟ-COOH	83[d]
4	$ClSiPh_3$	Ⓟ-$SiPh_3$	72
5	$ClPPh_2$	Ⓟ-PPh_2	71
6	$C_6H_{10}O$[e]	Ⓟ-$C(OH)C_5H_{10}$	51
7	C_6H_5CHO	Ⓟ-$CH(OH)C_6H_5$	100
8	$ClSiMe_3$	Ⓟ-$SiMe_3$	43
9	$BrCH_2CH_2Br$	Ⓟ-CH_2CH_2Br	17
10	C_4H_8O[f]	Ⓟ-$CH_2CH(OH)C_2H_5$	100

[a] *p*-Bromopolystyrene, 2.44 mmol of Br/g, DF = 0.31, 2% DVB cross-linking. [b] Elemental analyses. [c] FTIR and EI-MS. [d] Titration of COOH groups. [e] Cyclohexanone. [f] 1,2-Epoxybutane.

reactive calcium is independent of the calcium(II) halide used and therefore other anhydrous calcium(II) salts, such as $CaBr_2$ and $CaCl_2$, may be used to generate the calcium species. This dark calcium species appears to be reasonably soluble in THF. The work described in this paper utilizes the biphenylide generated calcium unless stated otherwise and, in some cases, a calcium–anthracenide reagent.

An excess (i.e., 0.5–1.5 equiv; based on starting halogen) of highly reactive calcium was added to cross-linked polystyrene resins containing halogen moieties (Br, Cl, F, CH_2Cl) at 0 °C and room temperature in THF under inert atmosphere conditions. Upon formation of the organocalcium reagent, the excess Ca* was removed from the polymer by filtration with Schlenk glassware and washed with THF. As shown in Table I, the transformation to the insoluble organocalcium reagent can occur quantitatively under a variety of reaction conditions as evidenced by elemental analysis of the polymer after aqueous quenching. Generally, the formation was carried out at 0 °C or room temperature in order to minimize any additional cross-linking that might occur. When the organocalcium reagents were isolated, red-brown solids were obtained. The reactivity of the organocalcium reagents was independent of the temperature at which it was formed. These reagents could be stored under nitrogen at room temperature for six months without appreciable loss in color or chemical reactivity.[18] When exposed to air, the solids immediately decomposed and changed color. Elemental analyses of the isolated organocalcium reagents confirmed the presence of calcium and the corresponding halogen but the analyses failed to quantitatively account for all of the elements. The exact nature of these organocalcium reagents is not known and may involve coordination or complexation with the solvent (THF) or lithium ions.

Functionalization of *p*-Bromopolystyrene. The reaction of a 2% cross-linked *p*-brompolystyrene (DF = 0.31) with highly reactive calcium (Scheme I) quantitatively afforded the organocalcium species after 36 h at room temperature. The reaction may be carried out without filtration of the excess Ca* from the polymer without significant effect to the functional yields. Reaction with $CO_{2(g)}$ at −45 °C followed by hydrolysis afforded the carboxylated product (entry 3, Table II) in an 83% functional yield.[19] The yield is comparable to yields previously reported involving lithiation[8] (80–95%) and Grignard formation[12a] (>70%) of *p*-bromopolystyrene. The addition of triphenylchlorosilane with the organocalcium species gave the silylated product (entry 4, Table II) in 72% yield. The arylcalcium species underwent Grignard-type reactions with benzaldehyde and cyclohexanone to yield the corresponding secondary and tertiary alcohols, respectively. The FTIR spectra of the alcohols yielded small broad OH stretches around 3400 cm^{-1} with sharp, intense peaks at 3640–4 cm^{-1} for "free" OH stretches.[20] This may be due to the site isolation of the alcohol within the polymer, and therefore only a small amount of intermolecular hydrogen bonding may be present. The former reaction yielded the secondary alcohol in a quantitative yield (entry 7, Table II).

Scheme II

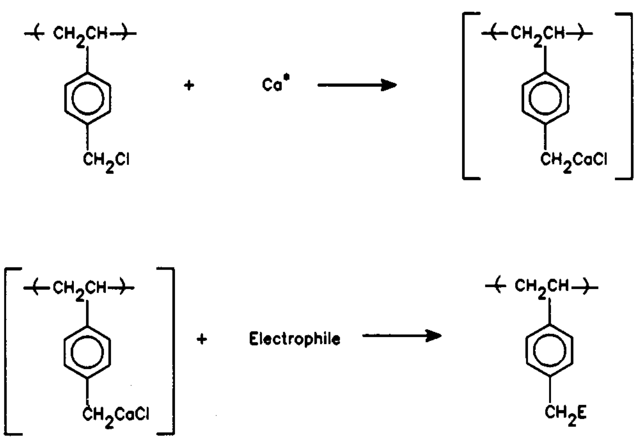

Table III. Reactions Involving Organocalcium Reagents Prepared from Chloromethylated Polystyrene[a] and Highly Reactive Calcium

entry	electrophile	polystyrene product	yield[b] (%)
1	H_2O	Ⓟ-CH_3	100
2	D_2O	Ⓟ-CH_2D[c]	
3	CO_2	Ⓟ-CH_2COOH	93[d]
4	$ClSiMe_3$	Ⓟ-CH_2SiMe_3	75
5	$C_6H_{10}O$[e]	Ⓟ-$CH_2C(OH)C_5H_{10}$	100
6	C_6H_5CHO	Ⓟ-$CH_2CH(OH)C_6H_5$	100
7	$ClPPh_2$	Ⓟ-CH_2PPh_2[c]	40

[a] Chloromethylated polystyrene, 1.06 mmol of Cl/g, DF = 0.11, 1% DVB cross-linking. [b] Elemental analyses. [c] 5.50 mmol of Cl/g, DF = 0.80, 2% DVB cross-linking; FTIR and EI-MS. [d] Titration of COOH groups. [e] Cyclohexanone.

The addition of a calcium species, prepared from CaI_2 and preformed lithium anthracenide, to *p*-bromopolystyrene (DF = 0.31) quantitatively afforded the arylcalcium species, and subsequent reaction with benzaldehyde at room temperature for 48 h yielded the secondary alcohol-containing polymer in an 80% yield. This dark calcium species seems to be reasonably soluble in THF and may be a calcium anthracene complex, similar in nature to the known magnesium anthracene complex.[21,12] Studies are currently underway to fully characterize this new and very reactive calcium species.

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(18) Transmetalation of the arylcalcium reagent, stored for 1 month under inert atmospheric conditions at room temperature, with CuCN·2LiBr followed by reaction with benzoyl chloride gave the ketone product (entry 1, Table V) in a 65% yield.

(19) Functional yield of the carboxylated polymer was based on acid–base titration: (a) Anand, L. C.; Takahasi, A.; Gaylord, N. G. *Macromol. Sym.* **1972**, *4*, 9. (b) See ref 8b.

(20) The unbonded or "free" hydroxyl group of alcohols and phenols absorbs strongly in the 3650–3584 cm^{-1} region. Silverstein, R. M.; Bassler, C. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley and Sons: New York, 1981.

(21) (a) Ramsden, H. E. U.S. Patent 3354190, 1967; *Chem. Abstr.* **1968**, *68*, 114744. (b) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1983**, *48*, 879. (c) Raston, C. L.; Salem, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1702. (d) Bogdanovic, B.; Liao, S.; Mynott, R.; Schlichte, K.; Westeppe, U. *Chem. Ber.* **1984**, *117*, 1378. (e) Harvey, S.; Junk, P. C.; Raston, C. L.; Salem, G. *J. Org. Chem.* **1988**, *53*, 3134. (f) Bogdanovic, B. *Acc. Chem. Res.* **1988**, *21*, 261 and references cited therein.

Table IV. Reactions Involving Organocalcium Reagents Formed from *p*-Chloropolystyrene[a] and *p*-Fluoropolystyrene[b] with Highly Reactive Calcium

entry	polystyrene polymer	electrophile	polystyrene product	yield[c] (%)
1	Ⓟ-Cl	H_2O	Ⓟ-H	100
2	Ⓟ-Cl	CO_2	Ⓟ-COOH	82[d]
3	Ⓟ-Cl	C_6H_5COCl	Ⓟ-COC_6H_5	26[e]
4	Ⓟ-Cl	CH_3COCl	Ⓟ-$COCH_3$	28[e]
5	Ⓟ-F	H_2O	Ⓟ-H	100
6	Ⓟ-F	CO_2	Ⓟ-COOH	78[d]
7	Ⓟ-F	$ClSiMe_3$	Ⓟ-$SiMe_3$	26
8	Ⓟ-F	C_6H_5COCl	Ⓟ-COC_6H_5	35[e]
9	Ⓟ-F	CH_3COCl	Ⓟ-$COCH_3$	59[e]
10	Ⓟ-F	C_6H_5CHO	Ⓟ-$CH(OH)C_6H_5$	25

[a] *p*-Chloropolystyrene, 3.75 mmol of Cl/g, DF = 0.45, 3% DVB cross-linking. [b] *p*-Fluoropolystyrene, 2.59 mmol of F/g, DF = 0.28, 3% DVB cross-linking. [c] Elemental analyses. [d] Titration of COOH groups. [e] Transmetalation with CuCN·2LiBr.

Functionalization of Chloromethylated Polystyrene. The addition of highly reactive calcium to a 1% cross-linked chloromethylated polystyrene (DF = 0.11) quantitatively generated the benzylic organocalcium species (Scheme II) after stirring for 6 h at 0 °C. Addition of $CO_{2(g)}$ at −45 °C followed by hydrolysis gave the corresponding carboxylic acid polymer (entry 3, Table III) in 93% yield.[19] The FTIR spectrum of the product confirmed the absence of the CH_2Cl precursor at 1266 cm^{-1} and the presence of the carboxyl group at 1711 cm^{-1}. This yield is in agreement with results reported by Fréchet et al.[12a,b] who reacted magnesium anthracene with chloromethylated polystyrene (DF = 0.15, 1% DVB cross-linking) and subsequent carboxylation with powdered dry ice to prepare the functionalized polymer in greater than 90% yield. The organocalcium species reacted with benzaldehyde and cyclohexanone in Grignard-type chemistry and quantitatively yielded the secondary and tertiary alcohols, respectively (entries 5 and 6, Table III).

Preformed lithium anthracenide reacted with calcium iodide to prepare a soluble calcium anthracene complex. This calcium species was added to chloromethylated polystyrene (DF = 0.11) and quantitatively yielded the organocalcium species when stirred for 6 h at 0 °C. Reaction of the organocalcium species with benzaldehyde gave the corresponding secondary alcohol in an 80% yield. Other reactions involving the biphenylide-based calcium are given in Table III.

Table V. Reactions of Calcium Cuprate[a] Reagents from *p*-Bromopolystyrene[b] with Various Electrophiles

entry	electrophile	polystyrene product	yield[c] (%)
1	C_6H_5COCl	Ⓟ-COC_6H_5	90
2	*p*-ClC_6H_4COCl	Ⓟ-COC_6H_4(*p*-Cl)	38
3	CH_3COCl	Ⓟ-$COCH_3$	100
4	$Br(CH_2)_3CN$	Ⓟ-$(CH_2)_3CN$	23
5	$Br(CH_2)_3CN$	Ⓟ-$(CH_2)_3CN$	39[d]
6	$Br(CH_2)_3CO_2Et$	Ⓟ-$(CH_2)_3CO_2Et$	60
7	C_6H_8O[e]	Ⓟ-C_6H_9O	90

[a] Transmetalation with CuCN·2LiBr. [b] *p*-Bromopolystyrene, 2.44 mmol of Br/g, DF = 0.31, 2% DVB cross-linking. [c] Elemental analyses. [d] Transmetalation with lithium 2-thienylcyanocuprate. [e] 2-Cyclohexen-1-one.

Table VI. Reactions of Calcium Cuprate[a] Reagents from Chloromethylated Polystyrene[b] with Various Electrophiles

entry	electrophile	polystyrene product	yield[c] (%)
1	C_6H_5COCl	Ⓟ-$CH_2COC_6H_5$	100
2	CH_3COCl	Ⓟ-CH_2COCH_3	100
3	$Br(CH_2)_3CN$	Ⓟ-$(CH_2)_4CN$	37
4	$Br(CH_2)_3CO_2Et$	Ⓟ-$(CH_2)_4CO_2Et$	80
5	C_6H_8O[d]	Ⓟ-$CH_2C_6H_9O$	100

[a] Transmetalation with CuCN·2LiBr. [b] Chloromethylated polystyrene, 1.06 mmol of Cl/g, DF = 0.11, 1% DVB cross-linking. [c] Elemental analyses. [d] 2-Cyclohexen-1-one.

Functionalization of *p*-Fluoropolystyrene and *p*-Chloropolystyrene. Except for highly reactive magnesium,[22] few metals undergo oxidative addition with aryl fluorides to form organometallic compounds.[23] Previous results from our group[17] involving the reaction of highly reactive calcium with aryl fluorides and chlorides encouraged us to prepare organocalcium reagents from polymers containing fluorine and chlorine. Significantly, the highly reactive calcium underwent oxidative addition with 3% cross-linked *p*-fluoropolystyrene[24] (DF = 0.28) and *p*-chloropolystyrene[24] (DF = 0.45) to quantitatively prepare the corresponding arylcalcium reagents upon addition at −78 °C for 1 h with warming to room temperature for 80 h (Scheme I). Reactions for shorter periods of time lead to only partial formation of the arylcalcium species. For example, the addition of the active calcium to *p*-fluoropolystyrene and stirring for 48 h at room temperature resulted in the formation of the arylcalcium species in a 71% yield upon aqueous quenching. Reaction with *p*-chloropolystyrene with active calcium for 48 h at room temperature afforded the arylcalcium species in an 81% yield.

The arylcalcium species (Scheme I) formed from *p*-fluoropolystyrene was found to react with chlorotrimethylsilane to give the silylated polymer in a 26% yield (entry 7, Table IV). Attempts to improve the functional yield of the silylated polymer were not successful. The addition of benzaldehyde to the arylcalcium reagent and subsequent reaction for 96 h yielded the secondary alcohol in 25% functional yield (entry 10, Table IV). When the reactivities of highly reactive calcium and copper toward *p*-fluoropolystyrene are compared, remarkable differences are found. The addition of highly reactive copper, prepared from the lithium naphthalenide reduction of CuI·PBu_3, resulted in no loss of fluorine from the polymer.[25] This reaction parallels that found when highly reactive copper was added to fluorobenzene.

The arylcalcium species formed from *p*-chloropolystyrene reacted with $CO_{2(g)}$ and gave the carboxylated polymer in an excellent yield (82%, entry 2, Table IV). Reaction of other electrophiles such as chlorotrimethylsilane, chlorodiphenylphosphine, and benzaldehyde resulted in low functional yields of the corresponding polymer products (10–25%). The reasons for these reduced yields compared to the *p*-bromopolystyrene are not clear.

Preparation and Reactions of Calcium Cuprate Reagents. The preparation of copper-derivatized polymers has been reported only twice in the literature. *p*-Bromopolystyrene, for example, was converted into the aryl cuprate by first forming the organolithium reagent by treatment with *n*-BuLi followed by the addition of a copper(I) salt.[12b] The direct metalation of *p*-bromopolystyrene using highly reactive copper, to prepare organocopper reagents, was reported by our group[26] to obtain functionalized polymers. The literature contains a wide spectrum

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(22) Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.

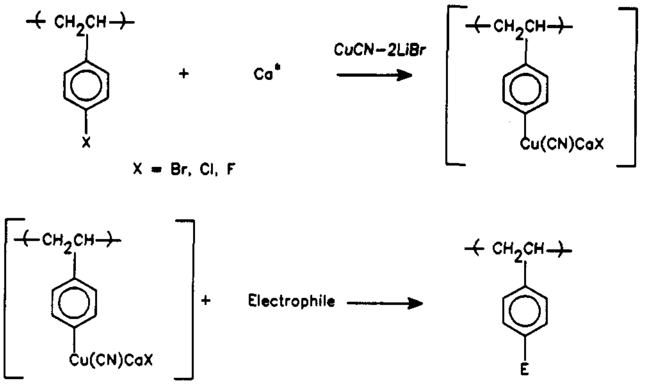
(23) Yu, S. H.; Ashby, E. C. *J. Org. Chem.* **1971**, *36*, 2123 and references cited therein.

(24) Polymers prepared following known literature procedures: Melby, L. R.; Strobach, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 450.

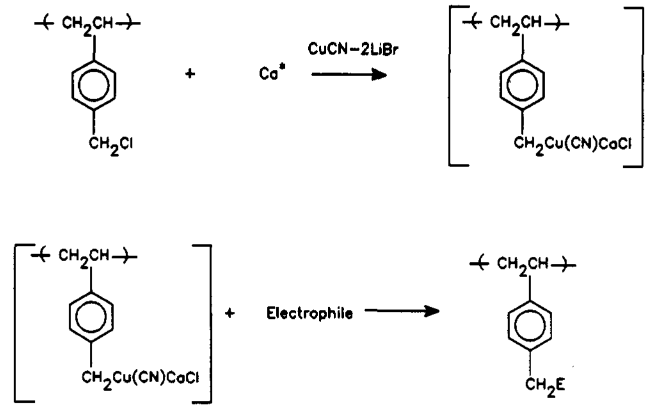
(25) O'Brien, R. A.; Chen, T.; Rieke, R. D. Unpublished results.

(26) O'Brien, R. A., Rieke, R. D. *J. Org. Chem.* **1990**, *55*, 788.

Scheme III



Scheme IV



of cuprates formed from lithium,[27] magnesium,[28] and zinc[29] derivatives and only recently has there been mention of calcium cuprates.[17] The copper-containing polymer reagents were readily prepared by transmetalation with a copper(I) salt. The resulting copper reagents displayed typical organocopper reactivity. Tables V and VI present some of the reactions of the calcium cuprate reagents with various electrophiles.

The aryl calcium cuprate formed from *p*-bromopolystyrene (DF = 0.31) (Scheme III) reacted with benzoyl chloride at −45 °C with warming to room temperature. This afforded the ketone-containing polymer (entry 1, Table V) in a 90% functional yield. FTIR, high-resolution EI-MS, and elemental analyses were used to characterize and quantitate the polymer product. The addition of highly reactive copper, prepared from $\mathrm{CuI{\cdot}PBu_3}$, to *p*-bromopolystyrene and subsequent addition of benzoyl chloride gave the same ketone product in a 70% yield.[26] It is interesting to note that reaction of the arylcalcium species with benzoyl chloride in the absence of CuCN·2LiBr also resulted in a 70% yield of the ketone product. When compared with the chemistry that occurs with monomers in solution, these results are drastically different. Reaction of an organocalcium reagent prepared from an organic halide and highly reactive calcium, with benzoyl chloride in the absence of a Cu(I) salt, afforded a complex mixture of products.[17] This chemistry is complicated by 1,2-additions to the initially formed ketones. Site isolation within the polymer allows the reaction to occur without the presence of a Cu(I) salt in a moderate yield. The site isolation either totally stops or at least slows the possible 1,2-additions which complicate the monomer chemistry.

Reaction of highly reactive copper, prepared from the cold-temperature reduction of CuCN·2LiBr,[30] with *p*-bromopolystyrene (DF = 0.31) for 4 h at −45 °C with warming to room temperature for 96 h afforded the corresponding organocopper reagent. Subsequent reaction with benzoyl chloride at −45 °C with warming to room temperature gave the functionalized polymer in an 82% functional yield with a 58% conversion to the organocopper species.[25]

Reaction of acetyl chloride with the calcium cuprate gave the ketone-containing polymer (entry 3, Table V) in a quantitative yield. When the reaction was carried out in one flask without filtration of the excess Ca* and 0.74 equiv of CuCN·2LiBr, the ketone product was formed in a 76% yield. Reaction of the calcium cuprate species with a functionalized alkyl halide, ethyl 4-bromobutyrate, gave the ester functionalized polymer (entry 6, Table V) in a 60% yield. Without transmetalation with CuCN·2LiBr, the product was formed in only 40% yield with 3% of the bromine-containing polymer found. Presumably, the formation of the bromine-containing polymer is a result of attack of the organocalcium reagent on the ester functionality. This type of attack was not seen from the calcium cuprate reagent when reacted with halides containing functionality. Transmetalation to the calcium cuprate reagents seems to enhance the reactivity of the copper-containing species toward cross-coupling reactions. Use of other copper(I) salts such as lithium 2-thienylcyanocuprate[31] led to a slight increase in yields (entry 5, Table V) and were not explored further.

The calcium cuprate reagents were also found to undergo conjugate 1,4-addition with α,β-unsaturated ketones. Reaction of the arylcalcium cuprate reagent with 2-cyclohexen-1-one afforded the conjugate addition product in 90% yield (entry 7, Table V).

The organocalcium species prepared from highly reactive calcium and chloromethylated polystyrene (DF = 0.11) was also transmetalated with CuCN·2LiBr at −45 °C for 2 h to generate the benzylic calcium cuprate species (Scheme IV). Addition of benzoyl chloride at −45 °C with warming to room temperature yielded the ketone-containing polymer in a quantitative yield (entry 1, Table VI). Without transmetalation, only a 60% yield of the ketone polymer was obtained. The calcium cuprate formed from the higher functionalized chloromethylated polystyrene (5.50 mmol of Cl/g, DF = 0.80, 2% DVB cross-linking) reacted with benzoyl chloride and afforded the ketone product in a moderate 61% yield.

The addition of highly reactive copper, prepared from cold temperature reduction of CuCN·2LiBr,[30] to chloromethylated polystyrene (DF = 0.11) and subsequent reaction with benzoyl chloride gave the ketone polymer in greater than 90% functional yield with a 61% conversion to the organocopper species.[25] The highly reactive copper

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(27) (a) Gilman, H.; Jones, R. G.; Woods, L. A. *J. Org. Chem.* **1952**, *17*, 1630. (b) Posner, G. H. *Org. React.* (*N.Y.*) **1972**, *19*, 1. (c) Normant, J. F. *Synthesis* **1972**, 63. (d) Lipshutz, B. H. *Tetrahedron Lett.* **1984**, *40*, 5005. (e) Lipshutz, B. H. *Synthesis* **1987**, 325.

(28) (a) Posner, G. H. *Org. React.* (*N.Y.*) **1975**, *22*, 253. (b) Collman, J. P.; Hegadus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 682. (c) Normant, J. F. *Pure Appl. Chem.* **1978**, *50*, 709.

(29) (a) Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390. (b) Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *Tetrahedron Lett.* **1988**, *29*, 2395. (c) Zhu, L.; Wehmeyer, R. M.; Rieke, R. D. *J. Org. Chem.* **1991**, *56*, 1445. (d) Benzylic organometallics of zinc and copper: Berk, S. C.; Knochel, P.; Yeh, M. C. P. *J. Org. Chem.* **1988**, *53*, 5791. (e) Rao, S. A.; Knochel, P. *J. Am. Chem. Soc.* **1991**, *113*, 5735.

(30) Stack, D. E.; Dawson, B. T.; Rieke, R. D. *J. Am. Chem. Soc.* **1991**, *113*, 4672.

(31) Lithium 2-thienylcyanocuprate was purchased from Aldrich Chemical Co.; Lipshutz, B. H.; Koerner, M.; Parker, D. A. *Tetrahedron Lett.* **1987**, *28*, 945.

Table VII. Bifunctionalization of Polymers Utilizing Highly Reactive Calcium

entry	polystyrene polymer	electrophile	polystyrene product	yield[a] (%)
1	Ⓟ-$\mathrm{COC_6H_4}$(*p*-Cl)[b]	$\mathrm{ClSiMe_3}$	Ⓟ-$\mathrm{COC_6H_4SiMe_3}$	60
2	Ⓟ-$\mathrm{CH_2COC_6H_4}$(*p*-Br)[c]	$\mathrm{ClSiMe_3}$	Ⓟ-$\mathrm{CH_2COC_6H_4SiMe_3}$	36
3	Ⓟ-$\mathrm{COC_6H_4}$(*p*-Cl)[b]	$\mathrm{ClPPh_2}$	Ⓟ-$\mathrm{COC_6H_4PPh_2}$	10

[a] Elemental analyses. [b] Based on 0.93 mmol of Cl/g. [c] Based on 0.77 mmol of Br/g.

was added to the polymer at −45 °C for 4 h with warming to room temperature for 48 h.

The addition of a functionalized halide, ethyl 4-bromobutyrate, with the calcium cuprate afforded the ester-functionalized polymer (entry 4, Table VI) in an 80% yield. Under the same reaction conditions and without the addition of CuCN·2LiBr, only a 40% yield of the functionalized polymer was obtained with 2% of the bromine-containing polymer found. Reaction of the more functionalized chloromethylated polystyrene (DF = 0.80), under the same reaction conditions as above (with CuCN·2LiBr), gave the ester functionalized polymer in a 26% yield.

Transmetalation of the organocalcium reagent, stored for 1 month under inert atmosphere conditions at room temperature, with CuCN·2LiBr followed by reaction with benzoyl chloride afforded the ketone-containing product (entry 1, Table VI) in a 95% yield.

As with *p*-bromopolystyrene, this new chemical reactivity of the calcium cuprate reagent was explored with 1,4-conjugate addition reactions. Reaction of the calcium cuprate reagent with 2-cyclohexen-1-one afforded the conjugate addition product in a quantitative yield (entry 5, Table VI). The FTIR spectrum of the product yielded an intense peak for the carbonyl in the 1709–11 cm^{-1} region with loss of the chloromethyl peak at 1266 cm^{-1}. The same reaction was carried out except that the calcium cuprate was filtered using Schlenk glassware. Fresh THF was added, and 2-cyclohexen-1-one reacted to give the 1,4-addition product in a quantitative yield. The presence of the calcium seems to produce a more reactive organocopper species even though it may be in trace amounts after filtration from the polymer.

Isolation of the calcium cuprate reagents, formed from *p*-bromopolystyrene and chloromethylated polystyrene, gave dark brown solids. Elemental analyses of the solids showed the presence of copper and nitrogen (from CuCN) but not calcium (within detection limits of 0.20%). The analyses accounted for about 94–95% of the total elements. These results suggest that the calcium can be removed by washing from the polymer and that the copper is bound to a carbon on the polymer.

Bifunctional Polymers Utilizing Highly Reactive Calcium. The addition of highly reactive calcium to a 4-chlorobenzophenone derivatized polymer (entry 2, Table V) and subsequent addition of chlorotrimethylsilane afforded the silylated product (entry 1, Table VII) in a 60% yield. The FTIR spectrum of the polymer showed the presence of peaks at 1251 and 758 cm^{-1} for the Si–C bonds and at 1664 cm^{-1} for the carbonyl. Elemental analyses of the product confirmed the complete loss of the chlorine from the polymer.

In summary, highly reactive calcium has been added to halogenated polystyrene resins to prepare organocalcium reagents. This soluble calcium will undergo oxidative addition to bromide-, chloride-, and fluoride-containing polymers and react with a variety of electrophiles to yield functionalized polymers. Transmetalation with CuCN·2LiBr yields the corresponding calcium cuprate reagents. These calcium cuprates undergo cross-coupling with acid chlorides to generate ketones and react with functionalized halides, as well as undergo 1,4-conjugate addition to 2-cyclohexen-1-one. The organocalcium reagents can be stored at room temperature for several months without appreciable loss in color or chemical reactivity. Bifunctionalization of the polymer can be achieved with the addition of highly reactive calcium to functionalized polymers containing halogens.

Experimental Section

General Aspects. FTIR (diffuse reflectance) were taken on an Analect RFX-65 FTIR spectrometer with KBr as the mull. Mass spectra were performed on Kratos MS-50 and MS-80 spectrometers by the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln. The polymer samples were heated ballistically to 400 °C. Solid-state ^{29}Si NMR were performed on a Chemagnetics (100-MHz) spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN) and Desert Analytics (Tuscon, AZ).

All manipulations were carried out under an atmosphere of argon on a dual manifold/argon system. The Linde prepurified-grade argon was further purified by passage over a BASF R3-11 catalyst at 150 °C, a phosphorus pentoxide column, and a column of granular potassium hydroxide. Lithium ribbon (28-mm wide × 0.38-mm thick), biphenyl, anthracene, naphthalene, and CaX_2 (X = I, Br, Cl) were weighed out and charged into reaction flasks under argon in a Vacuum Atmospheres Co. drybox. Tetrahydrofuran was distilled from Na/K alloy under an argon atmosphere immediately before use. Technical-grade wash solvents (MeOH, THF, and acetone) were used as received. Anhydrous calcium(II) iodide and bromide (99.5% purity) were purchased from Cerac, Inc., and calcium(II) chloride was purchased from Alfa Products. The calcium(II) salts were used without further purification. Copper(I) cyanide (99% purity) and lithium bromide (99% purity) were purchased from Aldrich Chemical Co. and stored in an argon drybox. All other reagents were used as received unless otherwise specified.

p-Bromopolystyrene was purchased from Lancaster Synthesis, LTD (2.44 mmol of Br/g, DF = 0.31, 2% DVB cross-linking, 200–400 mesh) and Fluka (5.47 mmol of Br/g, DF = 0.98, 2% DVB cross-linking, 200–400 mesh). Chloromethylated polystyrene was purchased from Kodak Chemicals (1.06 mmol of Cl/g, DF = 0.11, 1% DVB cross-linking, 200–400 mesh) and Lancaster Synthesis, LTD (5.50 mmol of Cl/g, DF = 0.80, 2% DVB cross-linking, 200–400 mesh). *p*-Chloropolystyrene (3.75 mmol of Cl/g, DF = 0.45, 3% DVB cross-linking, 200–400 mesh) and *p*-fluoropolystyrene (2.59 mmol of F/g, DF = 0.28, 3% DVB cross-linking, 200–400 mesh) were prepared from known literature procedures.[24] Acid–base titrations of the carboxylated polymers were performed following literature procedures.[19] The degrees of functionalization (DF) and functional yields of the polymers represent the fraction of aromatic rings that possess the desired functionalities. Low-temperature reactions were performed utilizing a Neslab endocal ULT-80 refrigerated circulating bath or using dry ice/acetonitrile or acetone slush baths. Deuterium oxide (99.7%) was purchased from Fischer Scientific. Workup of the polymers included filtering and washing with portions of H_2O, THF, MeOH, and acetone as well as drying. All polymers were dried under vacuum for 24 h at room temperature and/or at 80–100 °C for 24–48 h (when oxygen was analyzed).

Typical Procedure for the Preparation of Highly Reactive Calcium (Ca*). Lithium (2.05 mmol) and biphenyl (2.46 mmol) were stirred in freshly distilled THF (15 mL) at room temperature under argon until the lithium was completely consumed (ca. 2 h). To a well-suspended solution of CaI_2 (1.00 mmol) in THF (15 mL), the preformed lithium biphenylide was transferred via a cannula at room temperature. The solution of highly reactive calcium was stirred for 1 h at room temperature.

Preparation of Ⓟ-H (Ⓟ = polystyrene support). *p*-Bromopolystyrene (1.21 mmol of Br, based on 2.44 mmol of Br/g, DF = 0.31, 2% DVB cross-linking) was stirred in freshly distilled THF (30 mL) at room temperature for 24 h prior to use. Highly reactive calcium (3.02 mmol) was transferred via a cannula to the polymer at room temperature. The resulting dark solution was stirred for 48 h at room temperature. At this time the polymer was filtered and washed with THF (15 mL). Fresh THF (30 mL) was added to the polymer, and deionized water (15 mL) was added via a syringe. The solution was stirred for 44 h at room temperature, at which time the polymer was filtered and washed with 100-mL portions of H_2O (2×), THF (1×), MeOH (1×), acetone (1×), and MeOH (1×). The product was dried under vacuum for 24 h at room temperature and yielded 0.3419 g of a light brown powder. FTIR (diffuse reflectance): peaks absent at 1492, 1407, 1070, 1008, and 718 cm^{-1} for the aryl bromide precursor. Anal. Found: Br, 0.00.

Preparation of Ⓟ-D. Highly reactive calcium (2.82 mmol) was added to a solution containing *p*-bromopolystyrene (1.25 mmol of Br) and stirred for 36 h at room temperature. Deuterium oxide (5 mL) was added and stirred for 48 h at room temperature. Workup yielded 0.5257 g of a light brown powder. FTIR: peak observed at 2255 cm^{-1} for the C-D bond. HR EI-MS yielded fragments at *m/e* 105.0695 for $C_8H_7D^+$ (10.30), at *m/e* 131.0859 for $C_{10}H_{11}^+$ (2.89), and at *m/e* 104.0623 for $C_8H_8^+$ (26.90). Anal. Found: Br, 0.00.

Preparation of Ⓟ-COOH. Highly reactive calcium (2.92 mmol) was added to a solution containing *p*-bromopolystyrene (1.17 mmol of Br) and the resulting solution was stirred for 48 h at room temperature. Gaseous carbon dioxide was passed through a column of Drierite and bubbled into the solution at −45 °C for 2 h, 0 °C for 1 h, and at room temperature for 1 h. 0.5 N HCl (15 mL) was added to the reaction and the solution stirred for 30 min at room temperature. The polymer was filtered and washed with portions of 0.5 N HCl, THF, and MeOH. Drying yielded 0.3758 g of a tan powder. FTIR: peaks observed at 1733 and 1684 cm^{-1} for the COOH group.[32] Acid–base titrations yielded 2.03 mmol of COOH/g or 83% functional yield.

Preparation of Ⓟ-$SiPh_3$. Highly reactive calcium (3.02 mmol) was added to a solution containing *p*-bromopolystyrene (1.19 mmol of Br) and the resulting solution stirred for 40 h at room temperature. Chlorotriphenylsilane (3.38 mmol) in THF (10 mL) was added and stirred for 50 h at room temperature. Workup yielded 0.3419 g of a light brown powder. FTIR: observed peaks at 1248 and 758 cm^{-1} for the Si–C bond. HR EI-MS yielded fragments at *m/e* 259.0939 for $C_{18}H_{15}Si^+$ (3.40), *m/e* 130.0773 for $C_{10}H_{10}^+$ (3.21), and *m/e* 104.0625 for $C_8H_8^+$ (96.09). Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.76}(C_{26}H_{22}Si)_{0.22}$: Si, 3.82. Found: Si, 3.58. Functional yield = 72%.

Preparation of Ⓟ-PPh_2. Highly reactive calcium (3.04 mmol) was added to a solution containing *p*-bromopolystyrene (1.20 mmol of Br) and the resulting solution stirred for 48 h at room temperature. Chlorodiphenylphosphine (6.15 mmol) in THF (10 mL) was added at 0 °C and stirred for 1 h with warming to room temperature for 48 h. Acetone/H_2O (3:1) (20 mL) was added to the polymer and the mixture was stirred for 1 h at room temperature. Workup yielded 0.3590 g of a tan powder. FTIR: observed weak peaks at 1492, 1457, and 1005 cm^{-1} for the P–Ar bonds.[33] Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.76}(C_{20}H_{17}P)_{0.22}$: P, 4.69. Found: P, 4.38. Functional yield = 71%.

Preparation of Ⓟ-$C(OH)C_5H_{10}$. Highly reactive calcium (2.55 mmol) was added to a solution containing *p*-bromopolystyrene (1.04 mmol of Br) in THF (30 mL) and the resulting solution stirred for 48 h at room temperature. Cyclohexanone (5.67 mmol) in THF (10 mL) was added at −45 °C and the solution stirred for 1 h at −45 °C and warmed to room temperature for 70 h. Deionized water (20 mL) was added and the mixture stirred for 1 h at room temperature. Workup yielded 0.2912 g of a tan powder. FTIR: observed sharp peak at 3643 cm^{-1} for “free”” OH stretch,[20] broad OH stretch around 3460 cm^{-1}, and the C–O stretch at 1028 cm^{-1}. HR EI-MS yielded fragments at *m/e* 82.0792 for $C_6H_{10}^+$ (22.90), *m/e* 81.0721 for $C_6H_9^+$ (57.51), *m/e* 98.0733 for $C_6H_{10}O^+$ (19.25), *m/e* 104.0627 for $C_8H_8^+$ (11.74), and at *m/e* 129.0706 for $C_{10}H_9^+$ (2.28). Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.82}(C_{14}H_{18}O)_{0.16}$: C, 89.80; H, 8.07; O, 2.12. Found: C, 89.85; H, 7.46; O, 1.89. Functional yield = 51%.

Preparation of Ⓟ-$CH(OH)C_6H_5$. Highly reactive calcium (1.97 mmol) was added to a solution containing *p*-bromopolystyrene (1.31 mmol of Br) in THF (30 mL) and stirred for 48 h at room temperature. The polymer was filtered, fresh THF (30 mL) was added, and the mixture was cooled to −45 °C. Benzaldehyde (5.70 mmol) in THF (10 mL) was added at −45 °C and stirred for 4 h at −45 °C with warming to room temperature for 48 h. Deionized water (20 mL) was added to the polymer at −45 °C, and the mixture was allowed to warm to room temperature for 24 h. Workup yielded 0.3254 g of a tan powder. FTIR: observed sharp peak at 3641 cm^{-1} for “free”” OH stretch, broad OH stretch around 3400 cm^{-1} and C–O stretch at 1027 cm^{-1}. Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.67}(C_{15}H_{14}O)_{0.31}$: C, 89.14; H, 7.25; O, 3.60. Found: C, 88.86; H, 7.53; O, 3.74. Functional yield = 100%.

Anthracene-based Ca*: Lithium (6.07 mmol) and anthracene (6.99 mmol) were stirred in freshly distilled THF (15 mL) at room temperature under argon until the lithium was consumed (ca. 3 h). To a well-suspended solution of CaI_2 (2.87 mmol) in THF (15 mL) was transferred the preformed lithium anthracenide via a cannula at room temperature. The solution of highly reactive calcium was stirred for 1 h at room temperature. The calcium species was added to a solution containing *p*-bromopolystyrene (1.87 mmol of Br) in THF (30 mL) and stirred for 10 h at 0 °C. The polymer was filtered, fresh THF (30 mL) was added, and the mixture was cooled to −45 °C. Benzaldehyde (4.53 mmol) in THF (10 mL) was added at −45 °C, and the mixture was stirred for 4 h at −45 °C with warming to room temperature for 48 h. Deionized water (20 mL) was added to the polymer at room temperature, and the mixture was stirred for 24 h. Workup yielded 0.1402 g of a tan powder. The FTIR of the polymer was identical to above product. Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.726}(C_8H_7Br)_{0.006}(C_{15}H_{14}O)_{0.248}$: C, 90.35; H, 7.30; O, 3.01; Br, 0.36. Found: C, 89.82; H, 7.58; O, 3.21; Br, 0.38. Functional yield = 80%.

Preparation of Ⓟ-$SiMe_3$. Highly reactive calcium (1.93 mmol) was added to a solution containing *p*-bromopolystyrene (0.48 mmol of Br) in THF (30 mL) at room temperature for 48 h. Chlorotrimethylsilane (25.47 mmol) was added neat via a syringe and the solution stirred for 24 h at room temperature. Workup yielded 0.1048 g of a yellow-beige powder. FTIR: observed peaks at 1247 and 756 cm^{-1} for the Si–C bonds.[8b] Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.847}(C_{11}H_{16}Si)_{0.133}$: Si, 3.26. Found: Si, 3.08. Functional yield = 43%.

Preparation of Ⓟ-CH_2CH_2Br. Highly reactive calcium (3.20 mmol) was added to a solution containing *p*-bromopolystyrene (1.26 mmol of Br) in THF (30 mL) and the resulting solution stirred for 48 h at room temperature. 1,2-Dibromoethane (6.23 mmol) in THF (10 mL) was added at room temperature and stirred for 45 h at room temperature. Workup yielded 0.3845 g of a tan powder. FTIR: appearance of peaks at 1182 and 539 cm^{-1} for alkyl bromide.[8b] Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.927}(C_{10}H_{11}Br)_{0.053}$: Br, 3.83. Found: Br, 3.67. Functional yield = 17%.

Preparation of Ⓟ-$CH_2CH(OH)CH_2CH_3$. Polymeric arylcalcium reagent (4.85 mmol of Ⓟ-CaBr was prepared from *p*-bromopolystyrene and Ca*. Upon filtration of excess Ca*, THF (30 mL) was added and the solution cooled to −45 °C. 1,2-Epoxybutane (11.27 mmol) in THF (10 mL) was added at −45 °C, and the mixture was stirred for 2 h at −45 °C with warming to room temperature for 72 h. The reaction was quenched with deionized water (25 mL) and stirred for 30 min at room temperature. Workup yielded 1.4815 g of a tan powder. FTIR: observed sharp, intense peak at 3644 cm^{-1} for the “free” OH stretch, broad OH stretch around 3400 cm^{-1}, and the C–O stretch at 1028 cm^{-1}. Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.67}(C_{12}H_{16}O)_{0.31}$: C, 87.75; H, 8.35; O, 3.90. Found: C, 87.09; H, 7.72; O, 4.53. Functional yield = 100%.

Preparation of Ⓟ-CH_3. Highly reactive calcium (0.90 mmol) was added to a solution containing chloromethylated polystyrene (0.59 mmol of Cl, based on 1.06 mmol of Cl/g, DF = 0.11, 1% DVB cross-linking) in THF (30 mL) and stirred at 0 °C for 6 h. The polymer was filtered and yielded a red-brick colored solid. Fresh THF (30 mL) was added to the polymer followed by the addition of deionized water (20 mL) and the solution stirred for 24 h at room temperature. Workup yielded 0.4495 g of an off-white powder. FTIR: absence of peak at 1266 cm^{-1} for chloro-

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(32) Letsinger, R. L.; Kornet, M. J. *J. Am. Chem. Soc.* **1964**, *86*, 5163.

(33) Darling, G. D.; Fréchet, J. M. J. *J. Org. Chem.* **1986**, *51*, 2270.

methyl precursor. Anal. Found: Cl, 0.00.

Preparation of Ⓟ-CH_2D. Highly reactive calcium (11.34 mmol) was added to a solution containing chloromethylated polystyrene (2.82 mmol of Cl, based on 5.50 mmol of Cl/g, DF = 0.80, 2% DVB cross-linking) in THF (30 mL) and stirred for 96 h at room temperature. Deuterium oxide (10 mL) was added and the mixture stirred for 48 h at room temperature. Workup yielded 1.0622 g of a gray powder. FTIR: observed peak at 2260 cm^{-1} for C–D bond. HR EI-MS yielded fragments at *m/e* 119.0847 for $C_9H_9D^+$ (4.11), *m/e* 92.0615 for $C_7H_6D^+$ (9.49), *m/e* 130.0768 for $C_{10}H_{10}^+$ (1.58), *m/e* 118.0770 for $C_9H_{10}^+$ (2.39), and *m/e* 104.0617 for $C_8H_8^+$ (2.51). Anal. Found: Cl, 0.27 (99% loss).

Preparation of Ⓟ-CH_2COOH. Highly reactive calcium (1.15 mmol) was transferred to a solution containing chloromethylated polystyrene (0.71 mmol of Cl, based on 1.06 mmol of Cl/g) in THF (30 mL) and stirred for 6 h at 0 °C. The polymer was filtered, and fresh THF (30 mL) was added. Gaseous carbon dioxide was passed through a Drierite column and bubbled into the reaction flask at −45 °C for 2 h and 0 °C for 1 h, and the reaction was hydrolyzed with 1:1 H_2O/0.5 N HCl (20 mL). The solution was stirred for 1 h at 0 °C and warmed to room temperature for 12 h. Workup yielded 0.4836 g of an off-white powder. FTIR: observed peak at 1711 cm^{-1} for the COOH group.[12a] Acid–base titrations yielded 0.99 mmol of COOH/g or 93% functional yield.

Preparation of Ⓟ-CH_2SiMe_3. Highly reactive calcium (1.50 mmol) was added to a solution containing chloromethylated polystyrene (0.61 mmol of Cl, based on 1.06 mmol of Cl/g) in THF (30 mL) and stirred for 40 h at room temperature. Chlorotrimethylsilane (3.05 mmol) in THF (10 mL) was added and the solution stirred at room temperature for 48 h. Workup yielded 0.5503 g of a white powder. FTIR: observed peaks at 1248 and 755 cm^{-1} for the Si–C bond.[12a] Solid-state ^{28}Si NMR yielded a peak at 0.97 ppm for the TMS group. Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.88}(C_9H_{10})_{0.03}(C_{12}H_{18}Si)_{0.08}$: C, 89.97; H, 8.01; Si, 2.01. Found: C, 90.02; H, 7.80; Si, 1.75. Functional yield = 75%.

Preparation of Ⓟ-$CH_2C(OH)C_5H_{10}$. Highly reactive calcium (1.27 mmol) was added to a solution containing chloromethylated polystyrene (0.84 mmol of Cl, based on 1.06 mmol of Cl/g) in THF (30 mL) and stirred for 6 h at 0 °C. The polymer was filtered, and fresh THF (30 mL) was added. Cyclohexanone (2.24 mmol) in THF (10 mL) was added at −45 °C and the solution stirred for 1 h at −45 °C with warming to room temperature for 16 h. Deionized water (20 mL) was added to the polymer and the solution stirred for 1 h at room temperature. Workup yielded 0.7246 g of a white powder. FTIR: observed sharp peak at 3573 cm^{-1} for "free" OH stretch, broad peak around 3450 cm^{-1} for OH stretch and at 1030 cm^{-1} for the C–O stretch. Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.88}(C_{15}H_{20}O)_{0.11}$: C, 90.43; H, 8.04; O, 1.51. Found: C, 90.18; H, 7.89; O, 1.66. Functional yield = 100%.

Preparation of Ⓟ-$CH_2CH(OH)C_6H_5$. Highly reactive calcium (1.49 mmol) was added to a solution containing chloromethylated polystyrene (0.98 mmol of Cl, based on 1.06 mmol of Cl/g) in THF (30 mL) and the mixture stirred for 6 h at 0 °C. The polymer was filtered, and fresh THF (30 mL) was added. Benzaldehyde (4.26 mmol) in THF (10 mL) was added at −45 °C and the solution stirred for 1 h with warming to room temperature for 16 h. At this time, deionized water (20 mL) was added and stirred for 1 h at room temperature. Workup yielded 0.8900 g of a white powder. FTIR: observed sharp peak at 3642 cm^{-1} for "free" OH stretch, broad peak around 3550–3600 cm^{-1} for the OH stretch and at 1026 cm^{-1} for the C–O stretch. Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.88}(C_{16}H_{16}O)_{0.11}$: C, 90.87; H, 7.62; O, 1.49. Found: C, 91.04; H, 7.58; O, 1.86. Functional yield = 100%.

Anthracene-based Ca*: Highly reactive calcium (1.90 mmol) was prepared from lithium (3.82 mmol), anthracene (4.62 mmol), and CaI_2 (1.90 mmol) as described earlier. The calcium species was added to a solution containing chloromethylated polystyrene (1.28 mmol of Cl, based on 1.06 mmol of Cl/g) in THF (30 mL) and the resulting solution stirred for 6 h at 0 °C. The polymer was filtered, fresh THF (30 mL) added, and the mixture precooled to −45 °C. Benzaldehyde (3.99 mmol) in THF (10 mL) was added at −45 °C and stirred for 4 h at −45 °C with warming to room temperature for 48 h. Deionized water (20 mL) was added at room temperature and stirred for 1 h. Workup yielded 0.7198 g of a white powder. The FTIR of the polymer was identical to above product. Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.88}(C_9H_{10})_{0.022}(C_{16}H_{16}O)_{0.088}$: C, 91.11; H, 7.66; O, 1.22. Found: C, 91.78; H, 7.45; O, 1.60; Cl, 0.00. Functional yield = 80%.

Preparation of Ⓟ-CH_2PPh_2. Highly reactive calcium (3.08 mmol) was added to a solution containing chloromethylated polystyrene (1.51 mmol of Cl, based on 5.50 mmol of Cl/g, DF = 0.80) in THF (30 mL) and the resulting solution stirred for 48 h at room temperature. Chlorodiphenylphosphine (6.03 mmol) in THF (10 mL) was added at 0 °C for 1 h with warming to room temperature for 48 h. Acetone/H_2O (3:1) (20 mL) was added and the solution stirred for 1 h at room temperature. Workup yielded 0.200 g of a light yellow powder. FTIR: observed weak peaks at 1492, 1452, and 1001 cm^{-1} for P–Ar bonds. Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.18}(C_9H_{10})_{0.48}(C_{21}H_{19}P)_{0.32}$: C, 87.11; H, 7.21; P, 5.66. Found: C, 87.25; H, 7.15; P, 5.34. Functional yield = 40%.

Functionalized Polymers from Ⓟ-F and Ⓟ-Cl. Preparation of Ⓟ-COOH. From *p*-fluoropolystyrene: Highly reactive calcium (3.48 mmol) was added to a solution containing *p*-fluoropolystyrene (1.38 mmol of F, based on 2.59 mmol of F/g) in THF (30 mL) and stirred for 96 h at room temperature. Gaseous carbon dioxide was passed through a column of Drierite and bubbled into the solution at −45 °C for 2 h, 0 °C for 1 h and at room temperature for 1 h. 0.5 N HCl (15 mL) was added to the reaction and the mixture stirred for 30 min at room temperature. The polymer was filtered and washed with 0.5 N HCl, THF, and MeOH. Drying yielded 0.1474 g of a light gray powder. FTIR: observed peak at 1746 cm^{-1} for the COOH group and disappearance of aryl fluoride at 1230 cm^{-1}. Acid–base titrations yielded 2.02 mmol of COOH/g or 78% functional yield. Anal. Found: F, 0.00.

From *p*-chloropolystyrene: Highly reactive calcium (3.72 mmol) was added to a solution containing *p*-chloropolystyrene (1.46 mmol of Cl, based on 3.75 mmol of Cl/g) in THF (30 mL) and stirred for 96 h at room temperature. Gaseous carbon dioxide was passed through a column of Drierite and bubbled into the solution at −45 °C for 2 h, 0 °C for 1 h, and room temperature for 1 h. 1.0 N HCl (20 mL) was added and the mixture was stirred for 30 min at room temperature. Workup yielded 0.3002 g of a light gray powder. FTIR: observed peak at 1742 cm^{-1} for the COOH group and the disappearance of aryl chloride at 1090 cm^{-1}. Acid–base titrations yielded 3.07 mmol of COOH/g or 82% functional yield. Anal. Found: Cl, 0.00.

Preparation of Ⓟ-$SiMe_3$. From *p*-fluoropolystyrene: Highly reactive calcium (3.08 mmol) was added to a solution containing *p*-fluoropolystyrene (2.05 mmol of F) in THF (30 mL) and the mixture stirred for 120 h at room temperature. The polymer was filtered, fresh THF (30 mL) added, and the mixture cooled to 0 °C. Chlorotrimethylsilane (4.32 mmol) in THF (10 mL) was added at 0 °C and stirred for 1 h at 0 °C with warming to room temperature for 16 h. Workup yielded 0.3461 g of a white powder. FTIR: observed peaks at 1249 and 756 cm^{-1} for the Si–C bonds. Anal. Calcd for $(C_{10}H_{10})_{0.03}(C_8H_8)_{0.897}(C_{11}H_{16}Si)_{0.073}$: Si, 1.86. Found: Si, 1.66. Functional yield = 26%.

Preparation of Ⓟ-$CH(OH)C_6H_5$. From *p*-fluoropolystyrene: Highly reactive calcium (2.61 mmol) was added to a solution containing *p*-fluoropolystyrene (1.71 mmol of F) in THF (30 mL) at −45 °C for 4 h with warming to room temperature for 96 h. The polymer was filtered, fresh THF (30 mL) added, and the mixture cooled to −45 °C. Benzaldehyde (4.59 mmol) in THF (10 mL) was added at −45 °C and the solution stirred for 4 h at −45 °C with warming to room temperature for 96 h. Deionized water (20 mL) was added at room temperature and the solution stirred for 24 h. Workup yielded 0.3415 g of a yellowish-white powder. FTIR: observed sharp peak at 3650 cm^{-1} for "free" OH stretch, broad peak at 3400 cm^{-1} for OH stretch and C–O stretch at 1028 cm^{-1}. Anal. Calcd for $(C_{10}H_{10})_{0.03}(C_8H_8)_{0.90}(C_{15}H_{14}O)_{0.07}$: C, 91.39; H, 7.60; O, 1.00. Found: C, 91.15; H, 7.46; O, 0.85. Functional yield = 25%.

Preparation of Ⓟ-COC_6H_5. From *p*-fluoropolystyrene: Highly reactive calcium (3.52 mmol) was added to a solution containing *p*-fluoropolystyrene (2.33 mmol of F) in THF (30 mL) at −45 °C, and the resulting solution was gradually warmed with stirring at room temperature for 96 h. The polymer was filtered, fresh THF (30 mL) added, and the solution cooled to −45 °C. CuCN (3.68 mmol) and LiBr (7.25 mmol) in THF (10 mL) were added at −45 °C and the solution stirred for 4 h at −45 °C. Benzoyl chloride (5.63 mmol) in THF (10 mL) was added at −45 °C and the solution stirred for 2 h at −45 °C with warming to room temperature for 48 h. Workup yielded 0.7863 g of a light yellow powder. FTIR: observed peak at 1660 cm^{-1} for the carbonyl.[34] Anal. Calcd for $(C_{10}H_{10})_{0.03}(C_8H_8)_{0.872}(C_{15}H_{12}O)_{0.098}$: C, 91.24; H, 7.40; O, 1.36. Found: C, 91.27; H, 7.58; O, 1.03. Functional yield = 35%.

From *p*-chloropolystyrene: Highly reactive calcium (3.69 mmol) was added to a solution containing *p*-chloropolystyrene (2.48 mmol of Cl) in THF (30 mL) at −45 °C and the solution gradually warmed with stirring to room temperature for 96 h. The polymer was filtered, fresh THF (30 mL) added, and the solution cooled to −45 °C. CuCN (3.89 mmol) and LiBr (7.69 mmol) in THF (10 mL) were added at −45 °C and the solution stirred for 4 h at −45 °C. Benzoyl chloride (5.70 mmol) in THF (10 mL) was added at −45 °C and the solution stirred for 2 h at −45 °C with warming to room temperature for 48 h. Workup yielded 0.5922 g of a light yellow powder. FTIR: observed peak at 1660 cm^{-1} for the carbonyl. Anal. Calcd for $(C_{10}H_{10})_{0.03}(C_8H_8)_{0.853}(C_{15}H_{12}O)_{0.117}$: C, 91.06; H, 7.34; O, 1.60. Found: C, 90.46; H, 7.71; O, 1.20. Functional yield = 26%.

Preparation of Ⓟ-$COCH_3$. From *p*-fluoropolystyrene: Highly reactive calcium (1.72 mmol) was added to a solution containing *p*-fluoropolystyrene (1.13 mmol of F) in THF (30 mL) at −78 °C and the resulting solution stirred for 1 h at −78 °C with warming to room temperature for 80 h. The polymer was filtered, fresh THF (30 mL) added, and the solution cooled to −45 °C. CuCN (1.49 mmol) and LiBr (3.12 mmol) in THF (10 mL) were added at −45 °C and the solution stirred for 4 h at −45 °C. Acetyl chloride (6.49 mmol) in THF (10 mL) was added at −45 °C and the solution stirred for 4 h at −45 °C with warming to room temperature for 48 h. Workup yielded 0.2949 g of a light gray powder. FTIR: observed a peak at 1685 cm^{-1} for the carbonyl.[34] Anal. Calcd for $(C_{10}H_{10})_{0.03}(C_8H_8)_{0.805}(C_{10}H_{10}O)_{0.165}$: C, 90.08; H, 7.56; O, 2.35. Found: C, 90.14; H, 7.53; O, 2.27; F, 0.00. Functional yield = 59%.

From *p*-chloropolystyrene: Highly reactive calcium (2.18 mmol) was added to a solution containing *p*-chloropolystyrene (1.43 mmol of Cl) in THF (30 mL) at −78 °C and the solution stirred for 1 h at −78 °C with warming to room temperature for 80 h. The polymer was filtered, fresh THF (30 mL) added, and the solution cooled to −45 °C. CuCN (1.52 mmol) and LiBr (3.14 mmol) in THF (10 mL) were added at −45 °C and the solution stirred for 4 h at −45 °C. Acetyl chloride (4.40 mmol) in THF (10 mL) was added at −45 °C and the solution stirred for 4 h at −45 °C with warming to room temperature for 48 h. Workup yielded 0.1723 g of a light gray powder. FTIR: observed peak at 1682 cm^{-1} for the carbonyl. Anal. Calcd for $(C_{10}H_{10})_{0.03}(C_8H_8)_{0.844}(C_{10}H_{10}O)_{0.126}$: C, 90.57; H, 7.60; O, 1.83. Found: C, 88.55; H, 7.56; O, 1.60; Cl, 0.00. Functional yield = 28%.

Transmetalation Reactions with CuCN·2LiBr. Preparation of Ⓟ-COC_6H_5. Highly reactive calcium (1.95 mmol) was added to a solution containing *p*-bromopolystyrene (1.29 mmol of Br, based on 2.44 mmol of Br/g, DF = 0.31) in THF (30 mL) and stirred for 36 h at room temperature. The polymer was filtered, fresh THF (30 mL) was added, and the mixture cooled to −45 °C. CuCN (1.40 mmol) and LiBr (3.09 mmol) in THF (10 mL) were precooled to −45 °C and added to the polymer solution. The polymer was stirred for 2 h at −45 °C at which time benzoyl chloride (4.94 mmol) in THF (10 mL) was added and the solution stirred for 1 h at −45 °C with warming to room temperature over 48 h. Workup yielded 0.3918 g of a tan powder. FTIR: peak observed at 1663 cm^{-1} for the carbonyl and the absence of peaks at 1408, 1072, 1010, and 718 cm^{-1} for the aryl bromide precursor. HR EI-MS yielded fragments at *m*/*e* 105.0341 for $C_7H_5O^+$ (21.65), *m*/*e* 130.0783 for $C_{10}H_{10}^+$ (3.48), and at *m*/*e* 104.0623 for $C_8H_8^+$ (100). Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.701}(C_{15}H_{12}O)_{0.279}$: C, 89.76; H, 6.90; O, 3.33. Found: C, 89.38; H, 7.46; O, 3.24; Br, 0.00. Functional yield = 90%.

Preparation of Ⓟ-COC_6H_4(*p*-Cl). Highly reactive calcium (3.60 mmol) was added to a solution containing *p*-bromopolystyrene (1.39 mmol of Br) in THF (30 mL) and stirred for 48 h at room temperature. CuCN (2.62 mmol) and LiBr (4.86 mmol) in THF (10 mL) were precooled to −45 °C, added to the polymer solution, and the solution stirred for 2 h at −45 °C. 4-Chlorobenzoyl chloride (7.15 mmol) in THF (10 mL) was added and the solution stirred for 2 h at −45 °C with warming to room temperature for 41 h. Workup yielded 0.5409 g of a light tan powder. FTIR: observed peak at 1660 cm^{-1} for carbonyl and at 1090 cm^{-1} for the aryl chloride. Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.862}$-$(C_{15}H_{11}OCl)_{0.118}$: Cl, 3.45. Found: Cl, 3.37. Functional yield = 38%.

Preparation of Ⓟ-$COCH_3$. Highly reactive calcium (2.04 mmol) was added to a solution containing *p*-bromopolystyrene (1.34 mmol of Br) in THF (30 mL) and the resulting solution stirred for 36 h at room temperature. The polymer was filtered, fresh THF (30 mL) was added, and the solution cooled to −45 °C. CuCN (1.58 mmol) and LiBr (3.28 mmol) in THF (10 mL) were precooled to −45 °C and added to the polymer. The polymer was stirred for 2 h at −45 °C at which time acetyl chloride (4.70 mmol) in THF (10 mL) was added and the solution stirred for 1 h at −45 °C with warming to room temperature for 48 h. Workup yielded 0.3514 g of a tan powder. FTIR: observed peak at 1686 cm^{-1} for the carbonyl. Anal. $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.67}(C_{10}H_{10}O)_{0.31}$: C, 88.37; H, 7.41; O, 4.21. Found: C, 88.54; H, 7.79; O, 4.33. Functional yield = 100%.

Preparation of Ⓟ-$(CH_2)_3CN$. Highly reactive calcium (1.95 mmol) was added to a solution containing *p*-bromopolystyrene (1.29 mmol of Br) in THF (30 mL) and the resulting solution stirred for 48 h at room temperature. The polymer was filtered, fresh THF (30 mL) added, and the solution cooled to −45 °C. CuCN (1.51 mmol) and LiBr (3.38 mmol) in THF (10 mL) were precooled to −45 °C and added to the polymer and the solution stirred for 2 h at −45 °C. 4-Bromobutyronitrile (4.05 mmol) in THF (10 mL) was added at −45 °C and stirred for 1 h at −45 °C and the solution warmed to room temperature for 48 h. Workup yielded 0.2957 g of a light tan powder. FTIR: observed peak at 2247 cm^{-1} for the nitrile. Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.91}$-$(C_{12}H_{13}N)_{0.07}$: N, 0.91. Found: N, 0.80. Functional yield = 23%. Transmetalation with lithium 2-thienylcyanocuprate: Same reaction conditions with the addition of lithium 2-thienylcyanocuprate[31] (1.05 equiv to arylcalcium reagent, based on 0.25 M in hexanes) via a syringe. Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.86}$-$(C_{12}H_{13}N)_{0.12}$: N, 1.49. Found: N, 1.35. Functional yield = 39%.

Preparation of Ⓟ-$(CH_2)_3CO_2Et$. Highly reactive calcium (2.96 mmol) was added to a solution containing *p*-bromopolystyrene (1.18 mmol of Br) in THF (30 mL) and the resulting solution stirred for 48 h at room temperature. The solution was cooled to −45 °C at which time CuCN (1.91 mmol) and LiBr (4.04 mmol) in THF (10 mL) were added and the solution was stirred for 2 h at −45 °C. Ethyl 4-bromobutyrate (6.34 mmol) in THF (10 mL) was added at −45 °C, and the solution was stirred for 2 h at −45 °C and warmed to room temperature for 68 h. Workup yielded 0.3701 g of a tan powder. FTIR: peak observed at 1736 cm^{-1} for the ester carbonyl and at 1183 cm^{-1} for the C–O stretch. Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.794}(C_{14}H_{18}O_2)_{0.186}$: C, 87.34; H, 7.92; O, 4.73. Found: C, 87.73; H, 7.45; O, 4.88. Functional yield = 60%.

Preparation of Ⓟ-C_6H_9O. Highly reactive calcium (1.32 mmol) was added to a solution containing *p*-bromopolystyrene (0.90 mmol of Br) in THF (30 mL) and stirred for 48 h at room temperature. The polymer was filtered, fresh THF (30 mL) added, and the solution cooled to −45 °C. CuCN (1.42 mmol) and LiBr (2.80 mmol) in THF (10 mL) were added at −45 °C and the solution was stirred for 2 h at −45 °C. 2-Cyclohexen-1-one (2.50 mmol) in THF (10 mL) was added at −45 °C and the solution stirred for 2 h at −45 °C with warming to room temperature for 24 h. The polymer was quenched with 3 N HCl (8 mL) and stirred for 20 min. Workup yielded 0.3059 g of a tan powder. FTIR: observed a peak at 1709 cm^{-1} for the carbonyl.[35] Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.701}(C_{14}H_{16}O)_{0.279}$: C, 88.73; H, 7.87; O, 3.39. Found: C, 88.40; H, 7.72; O, 3.13. Functional yield = 90%.

Preparation of Ⓟ-$CH_2COC_6H_5$. Highly reactive calcium (1.44 mmol) was added to a solution containing chloromethylated polystyrene (0.58 mmol of Cl, based on 1.06 mmol of Cl/g, DF = 0.11) in THF (30 mL) and the solution stirred at room temperature for 40 h. CuCN (0.86 mmol) and LiBr (1.69 mmol) in

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(34) Fyles, T. M.; Leznoff, C. C. *Can. J. Chem.* **1976**, *54*, 935.

(35) Cyclohexanones absorb in the 1715–1710 cm^{-1} region. See ref 20.

THF (10 mL) were added at −42 °C, and the solution was stirred for 2 h at −42 °C. Benzoyl chloride (2.26 mmol) in THF (10 mL) was added at −42 °C, and the solution was stirred for 2 h at −42 °C and warmed to room temperature for 48 h. Workup yielded 0.5125 g of a light gray powder. FTIR: observed a peak at 1682 cm^{-1} for the carbonyl and disappearance of the chloride precursor at 1266 cm^{-1}. Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.88}(C_{16}H_{14}O)_{0.11}$: C, 91.05; H, 7.45; O, 1.50. Found: C, 91.40; H, 7.29; O, 1.18; Cl, 0.00. Functional yield = 100%.

Preparation of Ⓟ-CH_2COCH_3. Highly reactive calcium (0.97 mmol) was added to a solution containing chloromethylated polystyrene (0.65 mmol of Cl) in THF (30 mL) and stirred for 6 h at 0 °C. The polymer was filtered, fresh THF (30 mL) added, and the solution cooled to −45 °C. CuCN (0.85 mmol) and LiBr (1.59 mmol) in THF (10 mL) were added at −45 °C, and the solution was stirred for 2 h at −45 °C. Acetyl chloride (2.53 mmol) in THF (10 mL) was added at −45 °C, stirred for 1 h at −45 °C, and warmed to room temperature for 18 h. Workup yielded 0.5809 g of a light gray powder. FTIR: observed peak at 1713 cm^{-1} for the carbonyl. Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.88}(C_{11}H_{12}O)_{0.11}$: C, 90.70; H, 7.80; O, 1.59. Found: C, 90.85; H, 7.77; O, 1.94. Functional yield = 100%.

Preparation of Ⓟ-$(CH_2)_4CN$. Highly reactive calcium (0.97 mmol) was added to a solution containing chloromethylated polystyrene (0.61 mmol of Cl) in THF (30 mL) and stirred for 6 h at 0 °C. The polymer was filtered, fresh THF (30 mL) added and the solution cooled to −45 °C. CuCN (1.04 mmol) and LiBr (2.37 mmol) in THF (10 mL) were added at −45 °C, and the solution was stirred for 2 h at −45 °C. 4-Bromobutyronitrile (1.65 mmol) in THF (10 mL) was added at −45 °C and the solution stirred for 1 h at −45 °C and warmed to room temperature for 18 h. Workup yielded 0.2650 g of a brown powder. FTIR: observed a peak at 2250 cm^{-1} for the nitrile. Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.88}(C_9H_{10})_{0.069}(C_{13}H_{15}N)_{0.041}$: N, 0.52. Found: N, 0.50. Functional yield = 37%.

Preparation of Ⓟ-$(CH_2)_4CO_2Et$. Highly reactive calcium (0.93 mmol) was added to a solution containing chloromethylated polystyrene (0.60 mmol of Cl) in THF (30 mL) and stirred for 6 h at 0 °C. The polymer was filtered, fresh THF (30 mL) added, and the solution cooled to −45 °C. CuCN (0.99 mmol) and LiBr (2.29 mmol) in THF (10 mL) were added at −45 °C and stirred for 2 h at −45 °C. Ethyl 4-bromobutyrate (1.61 mmol) in THF (10 mL) was added at −45 °C and stirred for 2 h at −45 °C with warming to room temperature for 18 h. Workup yielded 0.4072 g of a yellow powder. FTIR: observed at peak at 1742 cm^{-1} for the ester carbonyl and at 1184 cm^{-1} for the C–O stretch. Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.88}(C_9H_{10})_{0.022}(C_{15}H_{20}O_2)_{0.088}$: C, 89.64; H, 7.90; O, 2.43. Found: C, 89.15; H, 7.70; O, 2.39. Functional yield = 80%.

Preparation of Ⓟ-$CH_2C_6H_9O$. Highly reactive calcium (0.84 mmol) was added to a solution containing chloromethylated polystyrene (0.56 mmol of Cl) in THF (30 mL) at 0 °C for 6 h. The polymer was filtered, fresh THF (30 mL) was added, and the solution cooled to −45 °C. CuCN (0.88 mmol) and LiBr (1.88 mmol) in THF (10 mL) were added at −45 °C and stirred for 2 h at −45 °C. 2-Cyclohexen-1-one (1.55 mmol) in THF (10 mL) was added at −45 °C and stirred for 2 h with warming to room temperature for 24 h. The polymer was quenched with 3 N HCl (8 mL) and stirred for 20 min. Workup yielded 0.4716 g of a light brown powder. FTIR: observed peak at 1709 cm^{-1} for the carbonyl. Anal. Calcd for $(C_{10}H_{10})_{0.01}(C_8H_8)_{0.88}(C_{15}H_{18}O)_{0.11}$: C, 90.69; H, 7.80; O, 1.51. Found: C, 90.44; H, 7.87; O, 1.33. Functional yield = 100%.

Bifunctionalization of Polymers. Preparation of Ⓟ-$COC_6H_4SiMe_3$. Highly reactive calcium (0.46 mmol) was added to a solution containing Ⓟ-COC_6H_4(*p*-Cl) (0.14 mmol of Cl, based on 0.93 mmol of Cl/g) in THF (30 mL) at room temperature for 72 h. Chlorotrimethylsilane (5.43 mmol) in THF (10 mL) was added at room temperature and stirred for 48 h. 1:1 H_2O/5% HCl (25 mL) was added and the mixture stirred for 1 h at room temperature. Workup yielded 0.0868 g of a tan powder. FTIR: observed peaks at 1251 and 758 cm^{-1} for the Si–C bonds and 1664 cm^{-1} for the carbonyl. Absence of aryl chloride precursor at 1090 cm^{-1}. HR EI-MS yielded fragments at *m/e* 73.0485 for $C_3H_9Si^+$ (8.14), *m/e* 105.0337 for $C_7H_5O^+$ (31.82), *m/e* 181.0648 for $C_{13}H_9O^+$ (4.50), and at *m/e* 104.0662 for $C_8H_8^+$ (73.82). Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.862}(C_{15}H_{12}O)_{0.047}(C_{18}H_{20}OSi)_{0.071}$: Si, 1.63. Found: Si, 1.56; Cl, 0.00. Functional yield = 60%.

Preparation of Ⓟ-$CH_2COC_6H_4SiMe_3$. Highly reactive calcium (0.44 mmol) was added to a solution containing Ⓟ-$CH_2COC_6H_4$(*p*-Br) (0.09 mmol of Br, based on 0.77 mmol of Br/g) in THF (30 mL) at room temperature and the solution stirred for 48 h at room temperature. Chlorotrimethylsilane (5.44 mmol) in THF (10 mL) was added and the solution stirred at room temperature for 48 h. Workup yielded 0.0929 g of a yellow-gray powder. FTIR: observed peaks at 1267 and 758 cm^{-1} for the Si–C bonds and 1687 cm^{-1} for the carbonyl. HR EI-MS yielded fragments at *m/e* 73.0488 for $C_3H_9Si^+$ (5.96), *m/e* 105.0345 for $C_7H_5O^+$ (13.67), *m/e* 130.0775 for $C_{10}H_{10}^+$ (2.63), and *m/e* 104.0628 for $C_8H_8^+$ (9.56). Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.18}$-$(C_9H_{10})_{0.69}(C_{16}H_{13}OBr)_{0.053}(C_{16}H_{14}O)_{0.017}(C_{19}H_{22}OSi)_{0.040}$: Si, 0.83. Found: Si, 0.77; Br, 3.03 (48% Br remaining). Functional yield = 36%.

Preparation of Ⓟ-$COC_6H_4PPh_2$. Highly reactive calcium (0.57 mmol) was added to a solution containing Ⓟ-COC_6H_4(*p*-Cl) (0.18 mmol of Cl, based on 0.93 mmol of Cl/g) in THF (30 mL) at room temperature and the resulting solution stirred for 72 h at room temperature. Chlorodiphenylphosphine (5.86 mmol) in THF (10 mL) was added and the solution stirred for 1 h at 0 °C with warming to room temperature for 48 h. Workup yielded 0.0500 g of a tan powder. FTIR: observed a peak at 1665 cm^{-1} for the carbonyl and weak peak at 1452 cm^{-1} for P–Ar bond. Anal. Calcd for $(C_{10}H_{10})_{0.02}(C_8H_8)_{0.862}(C_{15}H_{12}O)_{0.106}(C_{27}H_{21}PO)_{0.012}$: P, 0.31. Found: P, 0.25; Cl, 0.00. Functional yield = 10%.

Isolation of Intermediates.[36] **Organocalcium Species from *p*-Bromopolystyrene.** Highly reactive calcium (7.58 mmol) was added to a solution containing *p*-bromopolystyrene (5.08 mmol of Br, based on 2.44 mmol of Br/g) in THF (30 mL) and the resulting solution stirred for 36 h at room temperature. The organocalcium species was allowed to settle for 1 h at room temperature and then isolated using Schlenk glassware at room temperature and washed with THF (3×, 25 mL). The product was dried under vacuum at room temperature for 24 h and yielded 1.6955 g of a red-brown powder. Anal. Found: Ca, 3.78; Br, 5.09.

Organocalcium Species from Chloromethylated Polystyrene. Highly reactive calcium (4.59 mmol) was added to a solution containing chloromethylated polystyrene (3.18 mmol of Cl, based on 1.06 mmol of Cl/g) in THF (30 mL) and stirred for 6 h at 0 °C. The organocalcium species was allowed to settle for 1 h at 0 °C and then isolated using Schlenk glassware at room temperature and washed with THF (5×, 25 mL). The product was dried under vacuum at room temperature for 12 h and gave 0.0307 g of a red-brown powder. Anal. Found: Ca, 2.53; Cl, 1.34.

Calcium Cuprate Species from *p*-Bromopolystyrene. Highly reactive calcium (2.10 mmol) was added to a solution containing *p*-bromopolystyrene (1.41 mmol of Br, based on 2.44 mmol of Br/g) in THF (30 mL) and the resulting solution stirred for 48 h at room temperature. The polymer was filtered using Schlenk glassware, and fresh THF (30 mL) was added. The solution was cooled to −45 °C at which time CuCN (1.40 mmol) and LiBr (2.83 mmol) in THF (10 mL) were added. The resulting solution was stirred at −45 °C for 2 h. The polymer was filtered at −45 °C with warming to room temperature and dried under vacuum for 6 h at room temperature. Yielded 0.1595 g of a dark brown powder. Anal. Found: C, 77.35; H, 6.90; Cu, 7.85; N, 0.52; Br, 1.10; Ca, 0.20 (detection limit is 0.20%).

Calcium Cuprate Species from Chloromethylated Polystyrene. Highly reactive calcium (1.77 mmol) was added to a solution containing chloromethylated polystyrene (1.14 mmol of Cl, based on 1.06 mmol of Cl/g) in THF (30 mL) and the resulting solution stirred for 6 h at 0 °C. The polymer was filtered using Schlenk glassware, and fresh THF (30 mL) was added. The solution was cooled to −45 °C at which time CuCN (1.18 mmol) and LiBr (2.83 mmol) in THF (10 mL) were added. The resulting solution was stirred at −45 °C for 2 h. The polymer was then filtered at −45 °C with warming to room temperature using Schlenk glassware. The product was dried under vacuum for 8 h at room temperature and yielded 0.5034 g of a dark brown

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(36) No observed decomposition of intermediates, under inert atmospheric conditions, before combustion analysis.

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powder. Anal. Found: C, 82.78; H, 7.60; Cu, 3.76; N, 0.45; Cl, 0.27; Ca, 0.20 (detection limit is 0.20%).

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Registry No. BrLi, 7550-35-8; copper cyanide, 544-92-3.

Formylation of Aromatic Compounds with CO in HSO_3F-SbF_5 under Atmospheric Pressure

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The formylation of aromatic compounds such as benzene, toluene, xylenes, mesitylene, indan, tetralin, fluorobenzene, chlorobenzene, and bromobenzene was carried out in HSO_3F-SbF_5 under atmospheric CO pressure at 0 °C. In HSO_3F-SbF_5, both formylation and sulfonation took place to give formyl and sulfonyl compounds. In the case of alkylbenzenes, including toluene, xylenes, mesitylene, and tetralin, formylalkylbenzenesulfonyl fluorides, new compounds, were obtained by a one-pot reaction as well as alkylbenzaldehydes, alkylbenzenesulfonyl fluorides, and bis(alkylphenyl) sulfones. The direct introduction of a formyl and sulfonyl group was achieved in alkylbenzenes. The reaction path of the new compounds is a two-step reaction comprised of formylation as the first step and sulfonation as the second step. The product composition was strongly dependent on the acid strength of the HSO_3F-SbF_5 systems. The formyl compounds became predominant with increasing acidity of the HSO_3F-SbF_5 system. On the other hand, only sulfonyl compounds were produced when the acidity of the HSO_3F-SbF_5 system was low.

Introduction

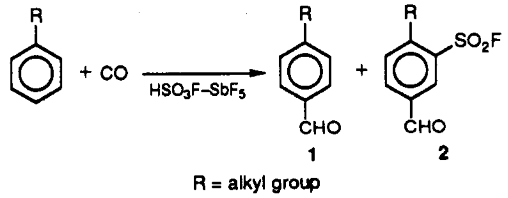
The formylation reactions of aromatic compounds with acid catalysts and CO are well-known as Gattermann–Koch reactions.[1] After Gattermann and Koch published their original paper concerning the synthesis of *p*-tolualdehyde from toluene and CO in the $HCl-AlCl_3-Cu_2Cl_2$ system,[2] other catalyst systems such as $HF-BF_3$,[3] $HF-SbF_5$,[4] $HF-CF_3SO_3H-BF_3$,[5,6] and CF_3SO_3H[7] have been extensively investigated for this reaction. In most cases, these formylations have been carried out under high pressure CO. There is continuing interest in the formylation of aromatic compounds with CO under milder conditions.

It has been demonstrated that HSO_3F is the strongest Brønsted acid and has become a widely used superacid solvent.[8] The systems such as HSO_3F-SbF_5 and $HSO_3F-SbF_5-SO_3$ have been recognized as the most highly acidic media;[9,10] however, the HSO_3F-SbF_5 system has not been used as a formylation catalyst. This paper investigates whether the HSO_3F-SbF_5 system can be used as a catalytic system in the formylation of aromatic compounds and reveals which specific reactions occur.

In this paper, we wish to report the formylation of aromatic compounds in HSO_3F-SbF_5 under atmospheric CO pressure at 0 °C and the formation of the new compounds, formylalkylbenzenesulfonyl fluorides as well as alkylbenzaldehydes, alkylbenzenesulfonyl fluorides, and bis(alkylphenyl) sulfones by a one-pot reaction. The composition of these four products based on reaction conditions was also investigated.

Results and Discussion

When alkylbenzene was slowly added to a mixture of HSO_3F and SbF_5 with vigorous stirring under atmospheric CO pressure at 0 °C, formylalkylbenzenesulfonyl fluoride **2** as well as alkylbenzaldehyde **1** was obtained by a one-pot reaction as follows:



Attempts to extend this reaction to a variety of aromatic

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(1) Olah, G. A. *Friedel-Crafts and Related Reaction*; Wiley-Interscience: New York, 1964; Vol. III, p 1153.

(2) Gattermann, L.; Koch, J. A. *Chem. Ber.* **1987**, *30*, 1622.

(3) (a) Takezaki, Y.; Sugita, N.; Kubo, H.; Kudo, K.; Yasutomi, T.; Yuasa, S. *Sekiyugakkaishi* **1964**, *7*, 564. (b) Fujiyama, S.; Kasahara, T. *Hydrocarbon Processing* **1978**, 147. (c) Gresham, W. F.; Tabet, G. E. *U.S. Pat.* 1949, 2485237.

(4) Olah, G. A.; Pelizza, F.; Kobayashi, S.; Olah, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 296.

(5) Olah, G. A.; Laali, K.; Farooq, O. *J. Org. Chem.* **1985**, *50*, 1483.

(6) Olah, G. A.; Ohannesian, L.; Arvanaghi, M. *Chem. Rev.* **1987**, *87*, 671.

(7) Booth, B. L.; El-Fekky T. A.; Noori, G. M. F. *J. Chem. Soc., Perkin Trans. 1* **1980**, 181.

(8) (a) Gillespie, R. J.; Peel, T. E.; Robinson, E. A. *J. Am. Chem. Soc.* **1971**, *93*, 5083. (b) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985.

(9) (a) Gillespie, R. J.; Peel, G. E. *J. Am. Chem. Soc.* **1973**, *95*, 5173. (b) Sommer, J.; Rimmelin, P.; Drankenberg, T. *J. Am. Chem. Soc.* **1976**, *98*, 2671.

(10) Gold, V.; Laali, K.; Morris, K. P.; Zdunek, L. Z. *J. Chem. Soc., Chem. Commun.* **1981**, 769.

0022-3263/92/1957-2677$03.00/0