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[*p*-((Trifluorovinyl)oxy)phenyl]lithium: Formation, Synthetic Utility, and Theoretical Support for a Versatile New Reagent in Fluoropolymer Chemistry

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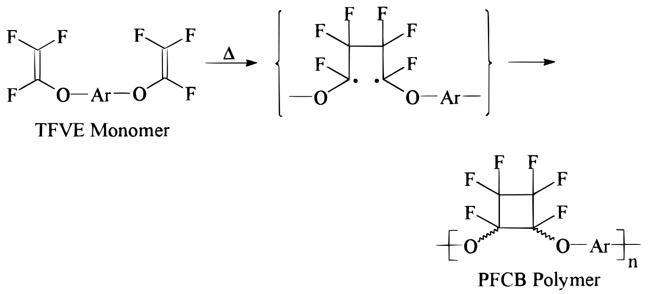
Summary: The metal−halogen exchange reaction of p-bromophenyl trifluorovinyl ether, p-$BrC_6H_4OCF{=}CF_2$ *(**1**), with tert-butyllithium in ether at −78 °C affords the title reagent,* p-$LiC_6H_4OCF{=}CF_2$ *(**2**), in solution. Subsequent addition of appropriate silicon, phosphorus, or organic electrophiles yields a wide variety of new trifluorovinyl ether monomers for fluoropolymer chemistry. Ab initio calculations (MP2/6-31G*//6-31G* level) indicate that the (trifluorovinyl)oxy substituent stabilizes anion **2** by approximately 10 kcal/mol relative to the methoxy analogue.*

Additions of carbon nucleophiles to fluorinated olefins are well-known and have been historically considered to be one of the best reactions in organofluorine chemistry.[1] Although less common, nucleophilic additions to fluorinated vinyl ethers were shown to proceed under even mildly basic conditions with relatively weak nucleophiles such as alcohols[2] and phenols.[3] These previous accounts, in fact, demonstrate the high efficiency of this reaction even where the electrophilic fluoroolefin is used as a monomer in a step growth polymerization scheme which requires near-complete functional group conversions. *We have found, however, that p-bromophenyl trifluorovinyl ether (**1**) undergoes facile halogen−metal exchange reactions affording versatile Grignard*[4] *and, as we report here, aryllithium reagents.* Organolithium compounds containing the electrophilic trifluorovinyl ether (TVFE) group have not been reported previously, whereas the Grignard reagent $CF_2{=}CFMgBr$ is easily generated and is reactive toward certain carbon electrophiles.[5]

Trifluorovinyl aromatic ether compounds are useful as monomers which undergo thermal cyclopolymerization to afford a new class of thermally stable perfluorocyclobutane (PFCB) aromatic polyethers (Scheme 1).[4,6]

Scheme 1



Traditional organic trifluorovinyl ether monomers were prepared from readily available bis- and tris(phenols) via fluoroalkyl ether formation followed by elimination.[6] Recent interest in inorganic hybrid PFCB polymers of this type, however, required new synthetic approaches, one of which is the delivery of the trifluorovinyl ether group to substrates via nucleophilic substitution.[4]

There has been considerable recent interest in the synthesis of hybrid fluorocarbon polymers[7] in which the incorporation of some fluorocarbon units and/or attached functional groups leads to useful properties such as low dielectric constants and high thermal stability. Fluorinated polyethers[8] and polyimides,[9] for example, have attracted significant attention in the quest for next-generation materials for a variety of microelectronics applications. Our initial entry into this area of hybrid perfluorocyclobutane polymers involved the in situ generation and subsequent silylation of the Grignard reagent from *p*-bromophenyl trifluorovinyl ether (**1**).[5] Further studies[10] indicated, however, that the Grignard

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(1) See for example: (a) Hudlicky, M. *Chemistry of Organic Fluorine Compounds*, 2nd ed.; Ellis Horwood: Chichester, England, 1976; pp 285−290, 407−410. (b) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973; pp 2−3, 148−170. (c) Chambers, R. D.; Mobbs, R. H. *Adv. Fluorine Chem.* **1965**, *4*, 50. (d) Miller, W. T.; Fried, J. H.; Godwhite, H. *J. Am. Chem. Soc.* **1960**, *82*, 3091.

(2) Hung, M.-H.; Farnham, W. B.; Feiring, A. E.; Rozen, S. *J. Am. Chem. Soc.* **1993**, *115*, 8954−8959.

(3) (a) Feiring, A. E.; Wonchoba, E. R. *J. Org. Chem.* **1992**, *57*, 7014−7017. (b) Fuss, A.; Koch, V. *Synthesis* **1990**, 604.

(4) Smith, D. W., Jr.; Babb, D. A. *Macromolecules* **1996**, *29*, 852 and references therein.

(5) Castelhaus, A. L.; Horne, S.; Taylor, G. J.; Billedeau, R.; Krantz, A. *Tetrahedron* **1988**, *44*, 5451 and references therein.

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(7) For general reviews, see: (a) *Fluoropolymers*; Wall, L. A. Ed.; Wiley: New York, 1972; Vol. XXV. (b) Feiring, A. E.; Imalzano, J. F.; Kerbow, D. L. *Trends Polym. Sci.* **1994**, *2*(1), 26. (c) Feiring, A. E. In *Organofluorine Chemistry: Principles and Commercial Applications*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum Press: New York, 1994; Chapter 15.

(8) See for example: (a) Feiring, A. E. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 1657. (b) Labadie, J. W.; Hedrick, J. L. *Macromolecules* **1990**, *23*, 5371. (c) Mercer, F.; Goodman, T.; Wojtowicz, J.; Duff, D. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *30*, 1767.

(9) See for example: (a) Wilson, D.; Stengenberger, H. D.; Hergenrother, P. M. *Polyimides*; Chapman and Hall: New York, 1990. (b) Cassidy, P. E.; Aminabhavi, M. T.; Farley, J. M. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29*, 365. (c) Arnold, F. E., Jr.; Cheng, S. Z. D.; Hsu, S. L. C.; Lee, C. J.; Harris, F. W.; Lau, S. *Polymer* **1992**, *33*, 5179. (d) Feiring, A. E.; Auman, B. C.; Wonchoba, E. R. *Macromolecules* **1993**, *26*, 2779. (e) Cheng, S. Z. D.; Arnold, F. E., Jr.; Li, F.; Harris, F. W. *Trends Polym. Sci.* **1993**, *1*(8), 243.

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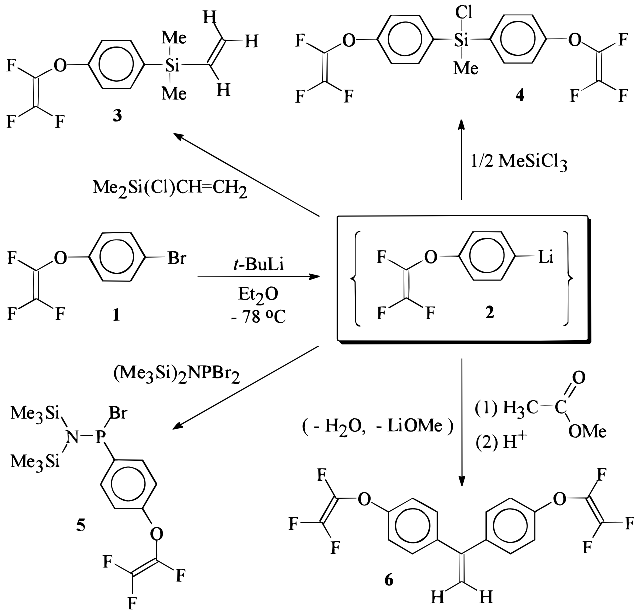
Scheme 2



reagent derived from **1** was insufficiently reactive toward many electrophiles, thus limiting its general synthetic utility. This prompted us to investigate the possibility of preparing the analogous organolithium derivative of aryl bromide **1**.

We find that the aryl bromide **1** undergoes smooth and quantitative metal–halogen exchange with *tert*-butyllithium in ether at −78 °C (Scheme 2), affording the desired intermediate **2** in solution.[11] Although it contains the highly reactive TFVE moiety, the organolithium derivative **2** is remarkably stable in ether solution at low temperature. *(**Caution**! When they are warmed above ca. −20 °C, solutions of **2** decompose very exothermically to yield complex mixtures of unidentified products.)* The conditions required to successfully prepare intermediate **2** are quite specific. For example, in contrast to its reactivity toward *tert*-butyllithium, **1** does not react with *n*-butyllithium below −20 °C in either THF or ether, even if tetramethylethylenediamine (TMEDA) is added. Moreover, in THF solution, *tert*-butyllithium appears to react preferentially with the solvent at low temperature rather than with the aryl bromide **1**.

The organolithium reagent **2** reacts readily in ether solution at low temperature with many different types of inorganic and organic electrophiles to afford a wide variety of new TFVE derivatives (Scheme 2). For example, the chlorosilanes $Me_2Si(Cl)CH{=}CH_2$ and $MeSiCl_3$ react with 1 or 2 equiv of **2** to afford the Si–vinyl and Si–Cl substituted organosilicon–TFVE derivatives **3** and **4**, respectively. Similarly, the dibromo(silylamino)phosphine $(Me_3Si)_2NPBr_2$ reacts smoothly with 1 equiv of **2** to produce the monosubstituted TFVE–phosphine product **5**. Illustrative of its reactivity toward organic electrophiles, addition of methyl acetate to a solution of **2**, followed by protonation, yields the tertiary alcohol $[p\text{-}F_2C{=}CFOC_6H_4]_2C(CH_3)OH$, which undergoes rapid dehydration to afford the bis-TFVE olefin derivative **6**. Compounds **3**–**6** are obtained in good yield as distillable, colorless liquids and have been fully characterized by NMR spectroscopy and elemental analysis.[12–15] In future publications, we will report on the use of these and many related TFVE compounds as synthetic precursors, polymerization monomers, and/or hydrosilation reagents in the synthesis of new types of PFCB–inorganic and –organic hybrid polymer systems.[10]

To further assess the remarkable formation and stability of anion **2**, the deprotonation energies at the 4-position of anisole, phenyl trifluorovinyl ether, protonated 4-methoxypyridine, and protonated 4-pyridinyl trifluorovinyl ether were determined computationally (Figure 1). The 4-substituted pyridines were chosen because they are isoelectronic with the corresponding 4-substituted aryl anions. The geometries and energetics of anisole, phenyl trifluorovinyl ether, and their corresponding anions (conjugate bases) and of 4-methoxypyridine, 4-pyridinyl trifluorovinyl ether, and their

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[10] Some new TFVE chemistry has been recently presented: Neilson, R. H.; Ji, J.; Narayan-Sarathy, S.; Oxley, J. D.; Smith, D. W., Jr. *Abstracts of Papers*, 213th National Meeting of the American Chemical Society, San Francisco, CA; American Chemical Society: Washington, DC, 1997; INORG 341.

[11] TFVE–Lithium Reagent 2. In a typical preparation, a 100 mL, three-neck, round-bottom flask, equipped with a magnetic stirring bar, a N_2 inlet, a rubber septum, and an addition funnel, was purged with N_2 and charged with aryl bromide **1** (7.6 g, 30 mmol) and dry ether (45 mL). The mixture was cooled to −78 °C ,and *t*-BuLi (17.7 mL, 31 mmol, 1.7 M in pentane) was added dropwise from the addition funnel. The mixture was then stirred for ca. 1 h at −78 °C prior to the addition of the next reactant.

[12] TFVE–Vinylsilane 3. On a 50 mmol scale, the chlorosilane $Me_2Si(CH{=}CH_2)Cl$ was added slowly via an addition funnel to a stirred solution of the lithium reagent **2**, prepared as above,[11] at −78 °C. The mixture was warmed slowly to room temperature and was stirred for at least 1 h. Following filtration and solvent removal, distillation afforded **3** as a colorless liquid (78% yield, bp 78 °C/3 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.61 (6H, s), 6.00 (1H, dd, J = 20, 3.9 Hz), 6.32 (1H, dd, J = 14.8, 3.9 Hz), 6.52 (1H, dd, J = 20.0, 14.8 Hz), 7.48 (2H, d, J = 8.5 Hz), 7.78 (2H, d, J = 8.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ −2.66 (Me_2Si), 115.4 (SiC^4) 115.6 (HC^3), 121.2 (=CH), 132.0 (=CF, m), 134.8 (=CH$_2$), 136.3 (HC^2), 147.8 (=CF$_2$, ddd, J = 279, 273, 62 Hz), 156.2 (OC^1). Anal. Calcd (found) for $C_{12}H_{13}OF_3Si$: C, 55.80 (55.12); H, 5.07 (5.35).

[13] TFVE–Chlorosilane 4. In a similar manner,[12] treatment of an ether solution of **2** (90 mmol) with $MeSiCl_3$ (45 mmol) afforded **4** as a distillable liquid (58% yield, bp 110 °C/0.07 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (3H, s), 7.41 (4H, d, J = 8.6 Hz), 7.89 (4H, d, J = 8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 1.21 (MeSi), 115.4 (SiC^4), 115.8 (HC^3), 132.0 (=CF, m), 136.4 (HC^2), 147.8 (=CF$_2$, ddd, J = 279, 273, 62 Hz), 156.2 (OC^1). Anal. Calcd (found) for $C_{17}H_{11}O_2F_6SiCl$: C, 48.07 (48.06); H, 2.61 (2.74).

[14] TFVE–Bromophosphine 5. On a 40 mmol scale, an ether solution of the dibromo(silylamino)phosphine $(Me_3Si)_2N{-}PBr_2$,[20] was cooled to −78 °C. A solution of lithium reagent **2** (40 mmol, prepared at −78 °C as above[11]) was transferred to a dry ice/acetone jacketed addition funnel and then added dropwise to the phosphine solution. The mixture was warmed to room temperature and stirred for 1 h. Ether was removed under reduced pressure, hexane (150 mL) was added to precipitate LiBr, the mixture was filtered, and the salt was washed with more hexane (2 × 30 mL). After solvent removal, distillation afforded **5** as a colorless liquid (73% yield, bp 103–113 °C/0.01 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.49 (18H, s), 7.4–8.0 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 3.6 (Me_3Si, d, J = 8.4 Hz), 115.7 (HC^3), 131.4 (HC^2, d, J = 20.5 Hz), 140.8 (PC,^{4} d, J = 55.3 Hz), 146.9 (=CF$_2$, ddd, J = 280, 274, 62 Hz), 155.7 (OC^1, m). ^{31}P NMR (120 MHz, $CDCl_3$): δ 149.1. Anal. Calcd (found) for $C_{14}H_{22}NOF_3Si_2PBr$: C, 37.84 (37.84); H, 4.99 (5.07).

[15] TFVE–Ethylene 6. On a 32 mmol scale, methyl acetate was added slowly to a stirred solution of the lithium reagent **2** at −78 °C. The reaction mixture was warmed slowly to room temperature and was then transferred to a separatory funnel and washed with 3% H_2SO_4 solution until the aqueous phase was acidic. The organic phase was then separated and dried over anhydrous $MgSO_4$. After filtration and solvent removal, distillation afforded **6** as a colorless liquid (62% yield, 90–108 °C/0.01 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.45 (2H, s), 7.10 (4H, d, J = 8.7 Hz), 7.35 (4H, d, J = 8.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.6 (=CH$_2$), 115.7 (HC^3), 129.8 (HC^2), 133.7 (=CF, ddd, J = 264, 48, 42 Hz), 138.1 (C^4), 147.0 (=CF$_2$, ddd, J = 280, 273, 63 Hz), 147.8 (C=), 154.8 (OC^1, q). Anal. Calcd (found) for $C_{18}H_{10}O_2F_6$: C, 58.08 (57.98); H, 2.71 (2.82).

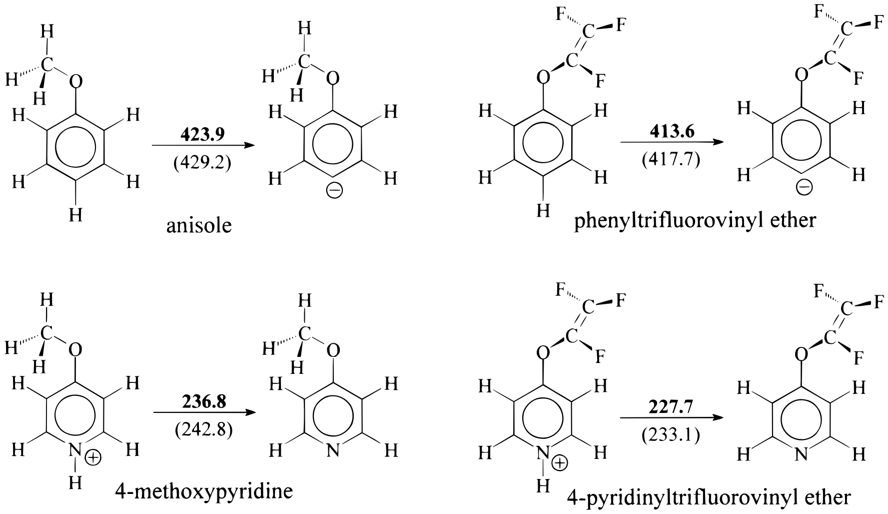

Figure 1. Calculated deprotonation energies. The numbers below the arrows (in parentheses) are the 6-31G* deprotonation energies (in kcal/mol) obtained from structures optimized using the 6-31G* basis set (i.e. 6-31G*//6-31G*). The numbers above the arrows (in boldface type) are MP2/6-31G* deprotonation energies, obtained from structures optimized using the 6-31G* basis set as well (i.e. MP2/6-31G*//6-31G*).

corresponding protonated derivatives (conjugate acids) were optimized using ab initio quantum mechanics at the Hartree–Fock level of theory[16] and the 6-31G* basis set.[17] To account for correlation energy, single-point energy calculations with second-order correlation energy corrections (MP2/6-31G*//6-31G*)[18] were also carried out on all of the relevant species. All of the calculations were performed using the molecular orbital program package Spartan.[19]

The computed deprotonation energies (Figure 1) were determined as the difference in energies between the "acid" and the corresponding conjugate base. For example, the computed deprotonation energy for anisole was obtained by calculating the energy difference between the parent anisole and the deprotonated analogue. A positive deprotonation energy indicates that the reaction is endothermic. Thus, deprotonation of anisole at the 4-position is endothermic by 429 kcal/mol according to the 6-31G* basis set. Substitution of the methyl group with the trifluorovinyl moiety lowers the deprotonation energy to 418 kcal/mol, suggesting that, *relative to the methyl group, the trifluorovinyl moiety stabilizes the anion by 11 kcal/mol. Inclusion of correlation energy correction (MP2/6-31G*) lowers the stabilization energy to 10 kcal/mol.* The computed deprotonation energy of protonated 4-methoxypyridine is 243 kcal/mol. Upon trifluorovinyl substitution, the deprotonation energy is lowered to 233 kcal/mol. This suggests that the trifluorovinyl species destabilizes the cationic site by 10 kcal/mol relative to the methyl group. Inclusion of correlation energy lowers the stabilization energy to 9 kcal/mol. These results, in addition to the qualitatively observed electron density map exhibiting clear charge delocalization concentrated on the trifluorovinyl ether group, clearly illustrate the decreased electrophilicity of the olefin and hence the decreased susceptibility to nucleophilic attack.

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(19) Spartan is a graphical quantum-mechanical program marketed by Wavefunction, Inc., 18401 Von Karman, No. 370, Irvine, CA 92715.

(20) The dibromophosphine $(Me_3Si)_2NPBr_2$ was prepared as described for the analogous $-PCl_2$ compound: Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1982**, *21*, 3568.