JOC The Journal of Organic Chemistry

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Synthesis of Protected Benzenepolyselenols

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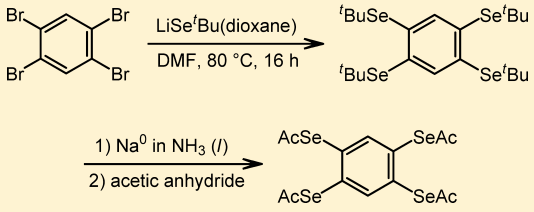
Supporting Information

ABSTRACT: Previously unknown benzenepolyselenols have been synthesized and isolated in their acetyl-protected form. The two molecules 1,3,5-tris(acetylseleno)benzene and 1,2,4,5-tetrakis(acetylseleno)benzene were synthesized by the reductive dealkylation in Na/NH_3 of 1,3,5-tris(*tert*-butylseleno)benzene and 1,2,4,5-tetrakis(*tert*-butylseleno)benzene, respectively. Hexakis(*tert*-butylseleno)benzene was also synthesized and structurally characterized by single-crystal X-ray diffraction, but it was not possible to isolate hexakis(acetylseleno)benzene. The synthetic methodology is likely to be useful in the synthesis of other areneselenols.



Benzenepolythiols have been fairly widely studied as electrically active components of materials and molecules. For example, 1,4-benzenedithiolate is the prototypical moiety for studies of single-molecule conductivity, usually between two gold electrodes.[1−3] Polynuclear metal complexes have been synthesized from 1,4-benzenedithiol,[4] 1,3,5-benzenetrithiol,[4] 1,2,4,5-benzenetetrathiol,[5−11] and benzenehexathiol.[12−15] Metal−organic polymers or networks, some of them semiconducting, have been synthesized with 1,4-benzendithiolate,[16−18] 1,2,4,5-benzenetetrathiolate,[17,19] and benzenehexathiolate[17] as the organic component. While both experimental[20,21] and theoretical[22−25] studies indicate that replacing the sulfur linking atoms with selenium would lead to higher single-molecule conductivity (although another theoretical study contradicts that finding[26]), and replacing sulfur by selenium in a hybrid organic−inorganic semiconductor is predicted to decrease the electronic band gap,[27] the chemistry of benzenepolyselenols is much less developed than that of benzenepolythiols. *Para*-substituted 1,4-benzenediselenol has been synthesized in both its unprotected form[28] and as the protected 1,4-di(acetylseleno)benzene.[29] *Ortho*-substituted 1,2-benzendiselenol (or 1,2-benzenediselenolate) has been synthesized by a variety of methods.[30−34] However, no benzeneselenols with three or more selenol groups (protected or unprotected) have been reported.

The most common route to arenepolythiols, the reductive cleavage of arenepoly(alkylthioethers) by sodium in liquid NH_3, was established in 1959.[35] The starting arenepoly(alkylthioethers)[36] are readily accessible through the nucleophilic aromatic substitution of arenepolyhalides with sodium alkylthiolates in solvents such as hexamethylphosphoramide (HMPA),[37−40] 1,3-dimethyl-2-imidazolidinone (DMI),[41] or dimethylformamide (DMF).[42,43] Scheme 1 shows this set of reactions for the benzenepolythiols.

The known benzenediselenols, 1,2-benzendiselenol and 1,4-benzenediselenol, were not synthesized by a route analogous to that in Scheme 1. Instead, 1,2-benzendiselenol (or 1,2-benzenediselenolate as an intermediate) has been synthesized by *ortho*-lithiation of benzeneselenol followed by reaction with 1 equiv of elemental selenium,[34] by the reaction of 1,2-dilithiobenzene with 2 equiv of selenium,[30] or by reduction of a 1,2-phenylenediselenide polymer.[32,33] It might be possible to iterate the *ortho*-lithiation route to produce 1,2,3-benzenetriselenol, 1,2,3,4-benzenetetraselenol, etc., but such a route would be inefficient and has been little explored.[44] The other reported benzenediselenol, 1,4-benzenediselenol, was synthesized by lithium−halogen exchange between 1,4-dibromobenzene and *tert*-butyllithium followed by treatment with elemental selenium.[28,29] However, that method is not viable for installing three or more selenol groups.[45]

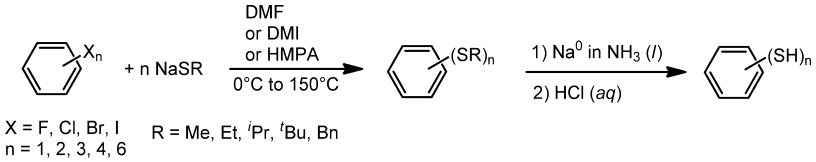
There is one published investigation in which a route analogous to the one in Scheme 1 was applied to the synthesis of benzeneselenols.[46] The alkyl selenide nucleophile was $LiSeCH_3$, and that led to a side reaction in which the methylselenide nucleophile adds to the methyl carbon of an already-formed aryl-$SeCH_3$ group, as shown in Scheme 2. For $LiSeCH_3$,this dealkylation is significantly faster than the second nucleophilic aromatic substitution,[46] while in a similar reaction of $NaSCH_3$ with 1,4-dichlorobenzene the two reactions occur at a comparable rates.[38] Once a dealkylation has occurred to form an arylselenide anion, the arene is deactivated and further nucleophilic aromatic substitution does not occur. We have found that the bulkier alkyl group of LiSe^tBu prevents the dealkylation reaction and allows the synthesis of benzenepoly(*tert*-butyl selenoethers), which can be subsequently dealkylated in Na^0/NH_3 to form (protected) benzenepolyselenols.

It was most convenient and effective to synthesize, isolate, and store a form of LiSe^tBu for use in subsequent reactions. Treatment of elemental selenium with 1 equiv of ^{t}BuLi in THF at −78 °C yields[47] LiSe^tBu(THF)$_x$, which is highly soluble in THF and too soluble in hexane for efficient recrystallization. We reasoned that 1,4-dioxane would form a less soluble, polymeric complex with LiSe^tBu. Evaporation of the volatiles

Received: August 14, 2012
Published: September 24, 2012

dx.doi.org/10.1021/jo301447h | *J. Org. Chem.* 2012, 77, 9397−9400

Scheme 1. Synthesis of Benzene Polythiols



Scheme 2. Reaction of $LiSeCH_3$ with 1,4-Dichlorobenzene

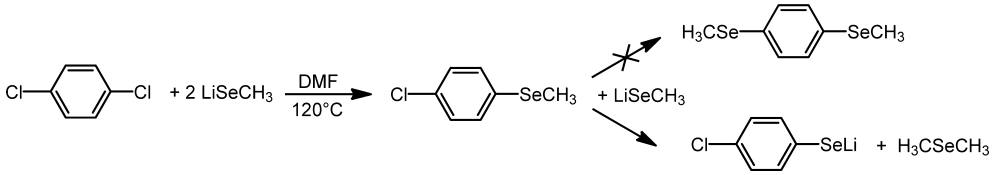
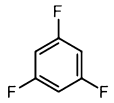
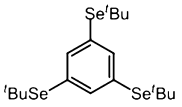
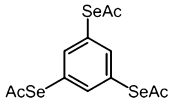
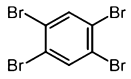
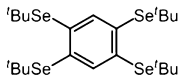
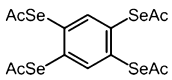
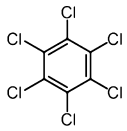
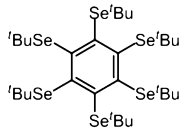


Table 1. Halobenzene Reactants, Reaction Conditions, and Yields

Starting Halobenzene	Rxn. Conditions	Selenoether	Protected Selenol
	3.5 LiSe^{t}Bu(dioxane) DMI, 80°C, 15 h	 41%	 85%
	4.2 LiSe^{t}Bu(dioxane) DMF, 80°C, 16 h	 29%	 69%
	7.0 LiSe^{t}Bu(dioxane) DMI, 22°C, 16 h	 60%	XXX

from a solution of $LiSe^tBu(THF)_x$ followed by addition of dioxane yields a homogeneous solution. Removal of excess dioxane and addition hexanes yields a white suspension of $LiSe^tBu$(dioxane), which was isolated by filtration and stored in a nitrogen-filled glovebox.

Reactions of polyhalobenzenes with the appropriate stoichiometry of $LiSe^tBu$(dioxane) were conducted in DMI or DMF at either 22 or 80 °C; reaction conditions and yields are summarized in Table 1. The identity of the halogen in the polyhalobenzenes was important. The synthesis of 1,3,5-benzenetri(*tert*-butyl selenide) from 1,3,5-trichlorobenzene in DMI gave an isolated yield of only 17%; the use of 1,3,5-trifluorobenzene improved the yield to 41%. The synthesis of 1,2,4,5-benzenetetra(*tert*-butylselenide) was possible only from 1,2,4,5-tetrabromobenzene: reactions using 1,2,4,5-tetrachlorobenzene or 1,2,4,5-tetrafluorobenzene in either DMF or DMI did not yield isolable product. Overall, yields of the benzenepoly(*tert*-butylselenoethers) were low to moderate. The products were isolated in pure form by simply filtering the DMI or DMF reaction mixture, from which the product precipitated over the course of the reaction. Analysis of the DMI/methanol or DMF/methanol filtrate showed the presence of a small amount of additional product in each case, but it was not practical to isolate and purify this additional product.

The two selenoethers 1,3,5-benzenetri(*tert*-butyl selenide) and 1,2,4,5-benzenetetra(*tert*-butyl selenide) were dealkylated by Na^0/NH_3 and then treated with acetic anhydride to give 1,3,5-benzenetri(selenoacetate) and 1,2,4,5-benzenetetra(selenoacetate), respectively, in good yield. Acetyl is a very convenient protecting group for areneselenols: it imparts air-stability on the areneselenol group, while it is easily hydrolyzed in the presence of an alkylamine (or stronger) base.

All attempts to synthesize benzenehexa(selenoacetate) from benzenehexa(*tert*-butylselenide) led to an insoluble orange solid. Treatment of the putative $Na_6C_6Se_6$ intermediate with CH_3I led to a mixture of products. Attempted crystallization of $Na_6C_6Se_6$ from water (the structure of the analogous $Na_6C_6S_6{\cdot}16H_2O$ is known[48]) yielded single crystals of $Na_2Se{\cdot}9H_2O$. It is possible that the steric congestion of six selenolate anions on $Na_6C_6Se_6$ leads to its instability, so we have investigated the single-crystal X-ray structure of benzenehexa(*tert*-butyl selenide).

A sample of $C_6(Se^tBu)_6$ was dissolved in hot heptane to form a red solution, which was slowly cooled to 22 °C. Data collection from a resulting red crystal yielded the structure shown in Figure 1. The bond distances for Se−C(*arene*) range from 1.93(1) to 1.95(1) Å and for Se−C(^{t}Bu) range from 1.98(1) to 2.01(1) Å. The C−Se−C bond angles range from 100.2(4) to 101.9(4)°. Steric interactions force the *tert*-butyl groups to alternating sides of the C_6 plane, as seen in Figure 1. In addition, the selenium atoms themselves deviate, on average, 0.18 Å from the mean plane of the C_6 core, all in the same

dx.doi.org/10.1021/jo301447h | J. Org. Chem. 2012, 77, 9397−9400

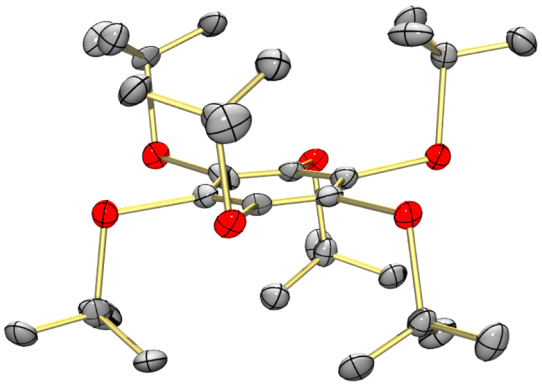


Figure 1. Single-crystal X-ray structure of $C_6(Se^tBu)_6$. Key: carbon, gray; selenium, red; hydrogen, not shown.

direction as their respective *tert*-butyl groups. The average Se−C−C−Se dihedral angle is 10°. It is most likely that those deviations from planarity are due to Se−Se interactions rather than interactions of selenium atoms with neighboring *tert*-butyl groups, as the compound $C_6(SePh)_6$ (Ph = phenyl) exhibits a similar alternating displacement of the selenium atoms from the C_6 plane.[49] Interestingly, in contrast, in hexaiodobenzene the iodine atoms deviate from the C_6 mean plane by only 0.046 Å on average.[50] In any case, when the selenoethers of $C_6(Se^tBu)_6$ are reduced to selenides in $C_6Se_6^{6-}$ the mutual repulsions of the anionic selenides may destabilize it to the point that it decomposes.

In conclusion, the synthesis of three benzene(selenoethers) and two acetyl-protected benzene(polyselenols) has been established. The synthetic methodology is likely to be useful in the synthesis of other areneselenols. Even when the halogen atoms of the haloarenes are not strongly mutually activating, as in 1,3,5-trifluorobenzene, the nucleophilic aromatic substitution to form the selenoethers is successful, which indicates that it is likely that this method can be extended to larger fluoroarenes in which the fluorine atoms are electronically isolated from each other.

EXPERIMENTAL SECTION

General Procedures and Materials. All reactions were carried out under N_2 in dry, oxygen-free solvents. Reagents and solvents were purchased from commercial suppliers and used as received, unless noted as follows. THF and dioxane were distilled from a purple sodium benzophenone solution, while hexane was distilled from sodium benzophenone tetraglyme. Dimethylformamide (DMF) and 1,3-dimethyl-2-imidazolidinone (DMI) were both distilled from P_2O_5 and stored over 3 Å molecular sieves. The benzenepoly(*tert*-butyl selenoethers) are air-stable, and the workup and subsequent handling were done without protection from air. The acylated products were worked up without protection from air but were stored under nitrogen after purification.

LiSe^{t}Bu(dioxane). To a suspension of selenium powder (3.00 g, 38.0 mmol) in 25 mL of THF at −78 °C was added ^{t}BuLi (1.7 M in pentane, 24 mL, 41 mmol) via syringe. An orange suspension began to form immediately. After 30 min, the cold bath was removed, and suspension was allowed to warm to 22 °C and stirred for 30 min. The volatiles were removed under reduced pressure, and the solid residue was dissolved in 25 mL of 1,4-dioxane to form a pale orange solution. The dioxane was removed under reduced pressure. Hexanes (~50 mL) was added, and stirring yielded a white suspension. The white solid was isolated by filtration and washed with hexanes. Yield of LiSe^{t}Bu(dioxane): 5.72 g, 65%. ^{1}H NMR (CD_3CN): δ 3.60 (s, 8H), 1.47 (s, 9H).

1,3,5-Tris(*tert*-butylseleno)benzene. DMI (2 mL) was added via syringe to LiSe^{t}Bu(dioxane) (500 mg, 2.16 mmol) to form an orange solution. Next 1,3,5-trifluorobenzene (80 mg, 0.61 mmol) was added, and the solution was heated to 80 °C for 15 h. The solution was cooled to 22 °C, and a white precipitate formed. Methanol (2 mL) was added, the suspension was cooled to −12 °C and stirred for 15 min, and the product was isolated by filtration and washed with 1 mL of cold methanol. Yield: 120 mg, 41%. Mp: 138−140 °C. ^{1}H NMR ($CDCl_3$): δ 7.97 (s, 3H), 1.42 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 147.4, 128.8, 44.1, 32.4. UV−vis in acetonitrile, 5.25×10^{-6} M: λ_{max} = 214 nm, $\varepsilon = 1.7 \times 10^5$ L·mol^{-1}·cm^{-1}, λ_{max} = 291 nm, $\varepsilon = 8.5 \times 10^3$ L·mol^{-1}·cm^{-1}. IR (Nujol cm^{-1}): 1536 (m), 1146 (s), 1020 (w), 882 (m), 801 (w), 742 (w), 691 (m), 666 (w). Anal. Calcd for $C_{18}H_{30}Se_3$: C, 44.73; H, 6.26; N, 0.00. Found: C, 44.76; H, 6.30; N, 0.23.

1,3,5-Tris(acetylseleno)benzene. Dry liquid ammonia was added to sodium (0.324 g, 14.1 mmol) and 1,3,5-tris(*tert*-butylseleno)-benzene (0.680 g, 1.41 mmol). The liquid ammonia was allowed to boil off through a bubbler over about 1 h. Degassed methanol (5 mL) was added via syringe, and the solution was stirred for 20 min. The methanol was then removed under vacuum and THF added to the orange residue. The suspension was stirred for 10 min, and then the THF was removed under vacuum. Fresh THF was added the residue, and then an excess of degassed acetic anhydride (2 mL) was added to the solution via syringe. After the solution was stirred for 1 h, the volatiles were removed under vacuum. Water (25 mL) was added to the residue, and the product was extracted with dichloromethane (3 × 25 mL). The combined organic layers were washed with water, dried over $MgSO_4$, and filtered. The solvent was removed under vacuum leaving a yellow oil. Yield of 1,3,5-tris(acetylseleno)benzene: 0.456 g, 85%. ^{1}H NMR ($CDCl_3$): δ 7.70 (s, 3H); 2.50 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 195.6, 142.6, 128.6, 34.3. HRMS (EI, magnetic sector mass analyzer): m/z calcd for $C_{12}H_{12}O_3Se_3$ 441.8290, found 441.8288.

1,2,4,5-Tetrakis(*tert*-butylseleno)benzene. DMF (5 mL) was added to 1,2,4,5-tetrabromobenzene (0.406 g, 1.03 mmol) and LiSe^{t}Bu(dioxane) (1.000 g, 4.33 mmol). The resulting orange solution was heated to 80 °C for 16 h and then cooled to room temperature. The white precipitate was isolated by filtration and washed sparingly with methanol. Yield of white 1,2,4,5-tetrakis(*tert*-butylseleno)-benzene: 0.188 g, 29%. Product can be recrystallized from hot 1:1 ethanol−methanol. Mp: 147−149 °C. ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 36H), 8.12 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 145.5, 137.6, 45.9, 32.6. UV−vis in acetonitrile, 3.11×10^{-5} M: λ_{max} = 229 nm, $\varepsilon = 2.5 \times 10^4$ L·mol^{-1}·cm^{-1}, λ_{max} = 286 nm, $\varepsilon = 1.1 \times 10^4$ L·mol^{-1}·cm^{-1}. IR (Nujol, cm^{-1}): 1407 (m), 1275 (w), 1231 (w), 1151 (s), 1099 (w), 1027 (s), 882 (m), 801 (w), 666 (w). Anal. Calcd for $C_{22}H_{38}Se_4$: C, 42.73; H, 6.19; N, 0.00. Found: C, 42.61; H, 6.33; N, 0.11.

1,2,4,5-Tetrakis(acetylseleno)benzene. Dry liquid ammonia was added to sodium (0.112 g, 4.85 mmol) and 1,2,4,5-tetrakis(*tert*-butylseleno)benzene (0.300 g, 0.485 mmol). The liquid ammonia was allowed to boil off through a bubbler over about 1 h. Degassed methanol (5 mL) was added via syringe to quench the excess sodium. The methanol was then removed under vacuum, and THF was added to the light pink residue. The suspension was stirred for 10 min, and then the THF was removed under vacuum and fresh THF was added. An excess of acetic anhydride (1 mL) was added to the solution via syringe, and after the suspension was stirred for 1.5 h, the solvents were removed under vacuum. Water (25 mL) was added, and the product was extracted with dichloromethane (4 × 25 mL). The combined organic layers were washed with water, dried over Na_2SO_4, and filtered. The solvent was removed under vacuum leaving a yellow solid. Yield of 1,2,4,5-tetrakis(acetylseleno)benzene: 0.189 g, 69%. Product can be recrystallized by partial evaporation of a solution in 1:1 CH_2Cl_2−heptane. Mp: 164−166 °C. ^{1}H NMR ($CDCl_3$): δ 2.49 (s, 12H), 8.09 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 194.9, 144.8, 135.6, 34.1. UV−vis in acetonitrile, 1.96×10^{-5} M: λ_{max} = 213 nm, $\varepsilon = 2.1 \times 10^4$ L·mol^{-1}·cm^{-1}, λ_{max} = 235 nm, $\varepsilon = 2.9 \times 10^4$ L·mol^{-1}·cm^{-1}. IR (Nujol cm^{-1}): 3414 (w), 1280 (m), 1096 (s), 1034 (m), 999 (w), 940 (m), 877 (m), 818 (w), 666 (w). Anal. Calcd for $C_{14}H_{14}O_4Se_4$: C, 29.92; H, 2.51; N, 0.00. Found: C, 29.53; H, 2.22; N, 0.12.

dx.doi.org/10.1021/jo301447h | J. Org. Chem. 2012, 77, 9397−9400

Hexakis(*tert*-butylseleno)benzene. DMI (8 mL) was added via syringe to hexachlorobenzene (0.317 g, 1.11 mmol) and LiSe^{t}Bu-(dioxane) (1.800 g, 7.78 mmol). After being stirred for several minutes at room temperature, the resulting brown solution became red-orange and a pink precipitate formed. After the solution was stirred for 16 h at room temperature, 100 mL of methanol was added and the solution was stirred at 0 °C for 30 min. The pink precipitate was isolated by filtration and washed with methanol. Yield of pink hexakis(*tert*-butylseleno)benzene: 0.590 g, 60%. The product is somewhat light-sensitive. Mp (under N_2): ~212−215 °C dec. ^{1}H NMR (C_6D_6): δ 1.56. ^{13}C NMR (C_6D_6): δ 33.06, 48.79, 128.31. UV−vis in hexanes: λ_{max} = 248 nm, $\varepsilon = 3.8 \times 10^4$ L·mol^{-1}·cm^{-1}; 276 nm (shoulder), $\varepsilon \sim 1.0 \times 10^4$ L·mol^{-1}·cm^{-1}; λ_{max} = 392 nm, $\varepsilon = 1.0 \times 10^3$ L·mol^{-1}·cm^{-1}; λ_{max} = 542 nm, $\varepsilon = 1.8 \times 10^2$ L·mol^{-1}·cm^{-1}. IR (Nujol cm^{-1}): 1295 (w), 1218 (w), 1150 (s), 1036 (w), 1010 (w), 666 (w). Anal. Calcd for $C_{30}H_{54}Se_6$: C, 40.55; H, 6.13; N, 0.00. Found: C, 40.10; H, 5.88; N: 0.13.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF and tabular formats; ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Steven Kelley for assistance in single-crystal X-ray data collection and reduction. This work was supported by the University of Alabama.

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