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Reaction of Hexachlorobenzene and (Pentachlorophenyl)lithium with α-Arylacetonitriles

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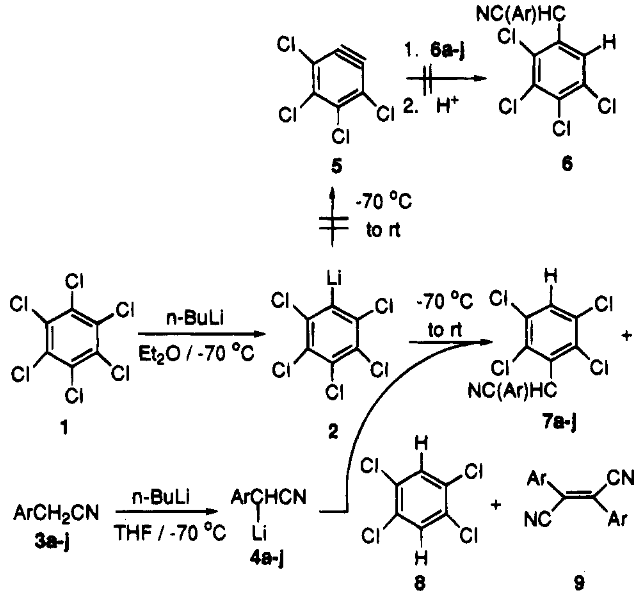
(Pentachlorophenyl)lithium (**2**) reacts with α-lithio-α-arylacetonitriles (**4**) at −70 °C to room temperature to supply α-aryl-α-(2,3,5,6-tetrachlorophenyl)acetonitriles **7**. Small amounts of 1,2,4,5-tetrachlorobenzene (**8**) and *trans*-1,2-dicyano-1,2-diarylethylenes **9** are also obtained; however, no α-tetrachloroarylated nitriles **6** from 3,4,5,6-tetrachlorobenzyne were detected. Similar treatment of hexachlorobenzene (**1**) and **4** afforded α-aryl-α-(2,3,4,5,6-pentachlorophenyl)acetonitriles **10**. The addition of **2** to **4** at tetrachlorobenzyne-generating temperatures (0−20 °C) gave a complex mixture containing mainly dimeric and polymeric materials; **6** was not found. A mechanism is proposed for the reaction of **2** and **4** which suggests that nitriles **7** are formed by the condensation of **2** and **4** via a four-centered transition state and that alkenes **9** are supplied by a base-mediated dimerization of α-chloro-α-arylacetonitriles **13**, formed by a lithium−chlorine exchange between **2** and **4**. Nitriles **10** most likely are provided from the reaction of **1** and **4** by the usual aromatic nucleophilic substitution pathway.

Introduction

Arynes contain bent acetylenic bonds, enforced by the geometry of the aromatic ring, which engenders a high degree of dienophilicity and electrophilicity into these highly reactive intermediates.[1] These properties have been exploited extensively in synthesis, especially in Diels−Alder cycloadditions and in arylations of carbon acids.[2] Tetrachlorobenzyne and tetrafluorobenzyne exhibit the greatest dienophilicity among arynes. Thus, in addition to yielding Diels−Alder adducts with typical dienes such as furan[3,4] *N*-methyl-,[5] and *N*-trimethylsilylpyrole,[6] they even engage in cycloadditions with aromatic compounds not usually thought of as dienes, namely, benzene,[7] 4-diisopropylbenzene,[8] and mesitylene.[9] In contrast, the electrophilic properties of these perhaloarynes, which should also be the strongest among the arynes, have not been studied,[10] and consequently they have not been taken advantage of in organic synthesis.[10] Because of our continuing interest in aryne arylation reactions,[11] we initiated an investigation of the electrophilic properties of tetrachlorobenzyne and report the results herein.

Scheme 1



a. Ar = C_6H_5
b. Ar = 3-MeO-C_6H_4
c. Ar = 4-MeO-C_6H_4
d. Ar = 3,4-$(MeO)_2$-C_6H_3
e. Ar = 3,4-(OCH_2O)-C_6H_3
f. 1-naphthyl
g. 2-thiophene
h. 3-thiophene
i. 3-Me-C_6H_4
j. 4-Me-C_6H_4

Results

Our initial plan for studying the electrophilic properties of tetrachlorobenzyne (**5**) is shown in Scheme 1. Accordingly, (pentachlorophenyl)lithium (**2**) and α-lithio-α-arylacetonitriles **4a−j** were to be prepared at −70 °C

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[1] Strozier, R. W.; Carmella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1340.

[2] For pertinent references, see: Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, 1967. Reinecke, M. G. *Tetrahedron* **1982**, *38*, 427. Levin, R. H. *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; J. Wiley: New York, 1978; Vol 1, pp 1−26; 1981; Vol 2, pp 1−14; 1985; Vol 3, pp 1−18. Gilchrist, T. L. *Carbenes, Nitrenes, and Arynes*; Appelton-Century-Croft: New York, 1969.

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[7] Hales, N. J.; Heany, H.; Hollinshead, J. H.; Singh, P. *Org. Synth.* **1979**, *59*, 71.

[8] Cook, J. D.; Fowler, N. J.; Wakefield, B. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 995.

[9] Heany, H.; Jablonski, J. M. *J. Chem. Soc. (C)* **1968**, 1895.

[10] In the only apparent report on the electrophilic properties of tetrahaloarynes, Penton *et al.* suggested that the formation of 2-hydrononafluorobiphenyl from the n-BuLi-mediated dimerization of bromopentafluorobenzene might involve 3,4,5,6-tetrafluorobenzyne. See: Penton, D. E.; Parks, A. J.; Shaw, D.; Massey, A. G. *J. Organometal. Chem.* **1964**, *2*, 437.

0022-3263/95/1960-1985$09.00/0

Table 1. Yields of Nitriles 7 and 10 and Alkenes 9 from the Reaction of (Pentachlorophenyl)lithium (2) and Hexachlorobenzene (1) with α-Lithio-α-arylacetonitriles 4

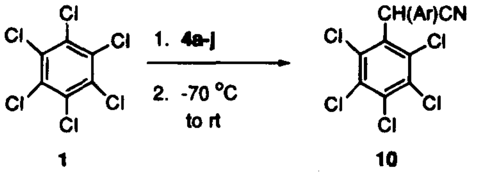
entry	solvent[a]	haloarene	α-lithio-α-arylnitrile	nitrile product, yield, %	*trans* alkene yield, %
1	A	**2**	**4a**	**7a**, 43	**9a**, 15
2	A	**2**	**4b**	**7b**, 51	**9b**, 18
3	A	**2**	**4c**	**7c**, 34	**9c**, 12
4	A	**2**	**4d**	**7d**, 51	*b*
5	A	**2**	**4e**	**7e**, 93	*b*
6	A	**2**	**4f**	**7e**, 40	**9e**, 16
7	A	**2**	**4g**	**7f**, 36	**9f**, 20
8	A	**2**	**4h**	**7g**, 56	**9g**, 15
9	A	**2**	**4i**	**7h**, 93	*b*
10	A	**2**	**4j**	**7j**, 72	*b*
11	B (A)	**1**	**4a**	**10a**, 90	
12	B (A)	**1**	**4b**	**10b**, 92 (88)	
13	B (A)	**1**	**4c**	**10c**, 80 (24)	
14	B (A)	**1**	**4d**	**10d**, 80	
15	B (A)	**1**	**4e**	**10e**, 80 (38)	
16	B (A)	**1**	**4f**	**10f**, 82 (67)	
17	B (A)	**1**	**4g**	**10g**, 85 (23)	
18	B (A)	**1**	**4h**	**10h**, 80 (42)	
19	B (A)	**1**	**4i**	**10i**, 85 (44)	
20	B (A)	**1**	**4j**	**10j**, 79 (42)	

[a] Solvent A = *ca*, 50:50 ether:THF; solvent B = ether. [b] Less than 5% yield of **9**.

from the reaction of n-BuLi with hexachlorobenzene (**1**) in ether and arylacetonitriles (**3a–j**) in THF, respectively. Solutions of **2** and **4a–j** were to be mixed and the resulting solution warmed to room temperature with the expectation that tetrachlorobenzyne (**5**) would be generated (0 °C to room temperature)[12] and subsequently trapped by the carbanions **4a–j** supplying α-aryl-α-(2,3,4,5-tetrachlorophenyl)acetonitriles **6**, after proton quenching. However, immediately upon mixing, the solutions developed a red color, which intensified during the remainder of the reaction. After quenching (aqueous ammonium chloride),[13] the expected aryne products **6** were not obtained, rather α-aryl-α-(2,3,5,6-tetrachlorophenyl)acetonitriles **7a–j** were supplied in 34–92% yields. Smaller amounts (5–20%) of 1,2,4,5-tetrachlorobenzene (**8**) and *trans*-1,2-dicyano-1,2-diarylethylenes **9** were also obtained. The isolated yields of the products are listed in Table 1 (entries 1–10).

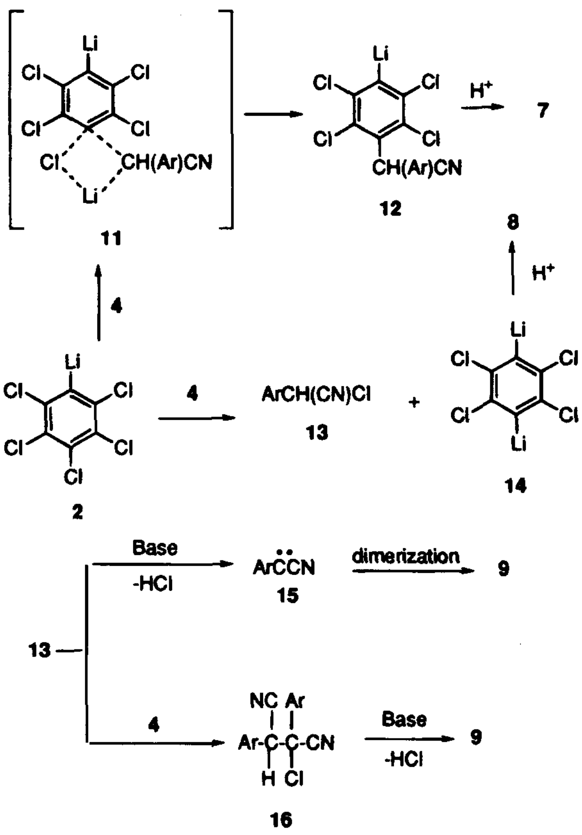
The IR, ^{1}H NMR, and ^{13}C NMR spectra of **7** and **9** are consistent with proposed structures. The structures of α-(3-thiophene-yl)-α-(2,3,5,6-tetrachlorophenyl)acetonitrile (**7h**),[14] and *trans*-1,2-dicyano-1,2-bis(4-methoxyphenyl)ethylene (**9c**) were further confirmed by X-ray diffractometry.[15]

Hexachlorobenzene (**1**) was found also to react with α-lithiated nitriles **4** under conditions similar to those used in the reaction of **2** and **4** to yield α-aryl-α-(2,3,4,5,6-pentachlorophenyl)acetonitriles (**10a–j**, eq 1). The nitriles **10a–j** were obtained in excellent yields (shown in Table 1, entries 11–20) when nitriles **4a–j** were prepared in ether. At −70 °C both **1** and **4a–j** are insoluble in ether, but upon warming to about −10 °C the suspension dissolved to give a deep red solution, from which a bright scarlet solid gradually precipitated while the reaction mixture was warmed to room temperature and stirred overnight. The yields of **10a–j**, however, were generally lower when **4a–j** was prepared in THF (in which they are soluble) owing to interfering addition and condensation reactions of nitriles **4a–j** and **10a–j** that frequently occur in THF at room temperature. The IR, ^{1}H NMR, and ^{13}C NMR spectra of **10a–j** were consistent with proposed structures, and the structure of α-(3-methoxyphenyl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile (**10b**) was further confirmed by X-ray diffractometry.[14]



eq. 1

Scheme 2



We attempted to generate tetrachlorobenzyne (**5**) in the presence of α-lithiated nitriles (**4a**) by adding its precursor **2** to **4a** at 10 °C. A complex mixture was obtained that contained mainly higher molecular weight materials, which appeared to be polychloro derivatives of biphenyls and polyphenyls, plus small amounts of **7a** (10%), **10a** (15%). However, the aryne-arylated product **6** was not found. Further attempts to generate aryne **5** in presence of anions **4** were not pursued.

Discussion

Scheme 2 shows a possible pathway for the formation of products **7–9** from the reaction of **2** and lithium derivatives **4**. Scheme 2 is based on the following considerations. The formation of *trans*-1,2-dicyano-1,2-

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[11] Biehl, E. R.; Khanapure, S. P. *Acc. Chem. Res.* **1989**, *22*, 275.

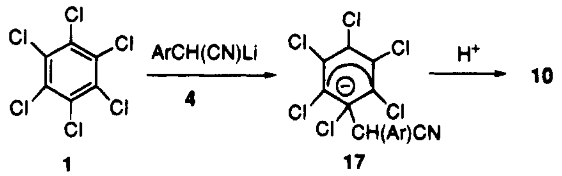
[12] Khanapure, S. P.; Crenshaw, L.; Reddy, R. T.; Biehl, E. R. *J. Org. Chem.* **1988**, *53*, 4195.

[13] If methanol or ethanol are used for quenching, the nitriles **7a–j** are partly oxidatively decyanated to ketones during workup of the resulting basic reaction solution.

[14] Zhang, H.-M.; Refat, H. M.; Biehl, E. R. *Acta Crstallogr.* **1995**, *C50*, in press.

[15] Zhang, H.-M.; Biehl, E. R.; Refat, H. M.; Faddo, A. A. *Acta Cryst.* **1995**, *C50*, in press.

Scheme 3



diarylethylenes **9** from **2** and **4** suggest α-(chloroaryl)acetonitriles **13** as intermediates. Makosza[16] has shown that α-(chlorophenyl)acetonitrile (**13a**) dimerizes to 1,2-dicyano-1,2-diphenylethylene (**9a**) in aqueous NaOH. It has been observed that α-(bromophenyl)acetonitrile dimerizes to **9a** when treated with alcoholic KOH.[17] α-(Chloroaryl)acetonitriles could be formed, along with 1,4-dilithiotetrachlorobenzene (**14**), by a lithium–chlorine exchange between **2** and **4**. Proton quench of **14** yields tetrachlorobenzene (**8**). Following Makosza suggestion,[16] the α-chloro derivatives **13** could either undergo α-dehydrochlorination to give carbene intermediates **15** which dimerize to **9**, or suffer nucleophilic attack by a carbanion **4** to give **16**, which could undergo β-dehydrochlorination to form **9**. We attempted to trap phenylcyanocarbene **9c** as its 4-bicyclo[4.1.0]heptane derivative by carrying out the reaction of **2** with α-lithio-α-phenylacetonitrile (**4c**) in the presence of cyclohexene. A very small amount of an oil (~6%) was isolated whose ^{1}H NMR revealed a multiplet centered around 0.8 ppm, which is consistent with proposed structure.

Due to the instability of **13** in highly basic media, the formation of nitrile products **7** should not involve **13** and the dilithio derivative **14**. In support of this, it was found that the reaction of **13a** and **14a** (prepared by literature procedures][19,20] afforded predominantly alkene **9a** (38%) and tetrachlorobenzene **8** (15%), but only trace amounts (<5%) of nitriles **7a**. α-(Bromophenyl)acetonitrile, which should be more prone than **13a** to exchange lithium,[21] was also found to give only alkene **9a** and **8** when treated with **14**. Thus the condensation of **2** and **4** must occur in one step process affording the lithium derivative **12**[21] and most likely proceeds through a four-centered transition state **11**.[22] The nitrile product **7** is subsequently formed by the protonation of **12** during aqueous workup.

As suggested in Scheme 3, the formation of aryl(pentachlorophenyl)acetonitriles **10** from the reaction of hexachlorobenzene (**1**) proceeds through a typical nucleophilic aromatic substitution pathway. This is the result of the stabilization of the Meisenheimer complex **18** by the cumulative inductive effect of the six chlorines.[23] Furthermore, the absence of alkenes **9** in these reactions argues against the intermediacy of α-chloro nitriles **13**.

In summary, we have shown that α-arylacetonitriles **4** react with both (pentachlorophenyl)lithim (**2**) and hexachlorobenzene (**1**) under mild conditions to yield novel α-aryl-α-(2,3,4,5,6-pentachloro- (**7**) and α-aryl-α-(2,3,5,6-tetrachlorophenyl)acetonitriles (**10**), respectively. The electrophilic properties of tetrachlorobenzyne (**5**), however, could not be assessed since the rate of generation of **5** from **2** in these reactions appears to be much slower than the rate of formation of the non-arynic products **7**.

Experimental Section

General Data. All reactions were done under a dry, oxygen-free nitrogen atmosphere, and the glassware was heated at 125 °C in an oven overnight prior to use. Tetrahydrofuran (THF) and diethyl ether solvents were passed through a column containing neutral alumina and then refluxed in the presence of sodium benzophenone ketyl until a permanent blue color was achieved. The arylacetonitriles, hexachlorobenzene, and n-BuLi were obtained commercially and were distilled or recrystallized prior to use. Melting points were taken on an electrochemical apparatus and are uncorrected. FTIR spectra were obtained on samples dissolved in CHCl$_3$, whereas NMR spectra of CDCl$_3$ solutions were recorded on a 200 MHz spectrometer; chemical shifts are related to TMS as internal standard. The elemental analyses were performed by the SMU Chemistry Analytical Services.

General Procedure for the Reaction of (Pentachlorophenyl)lithium (2) with α-Lithio-α-arylacetonitriles 4. To a stirred suspension of hexachlorobenzene [**1**, 2.82 g, 10 mmol) and 40 mL of ether at −70 °C was added n-butyllithium (10 mmol, 4 mL of 2.5 M soln) dropwise and the stirring continued at −70 °C. The suspension dissolved within 30 min to give a clear, yellow solution, indicating the conversion of **1** to **2**. In a separate flask, 11 mmol of the α-lithiated nitrile **4** was prepared by adding 11 mmol (4.4 mL of 2.5 M soln) of n-butyllithium to 11 mmol of the appropriate nitrile (**5**) dissolved in 40 mL of THF at −70 °C, followed by additional stirring (at least 2 h) until the preparation of **2** in the other flask was complete. The THF solution of **4** was then cannulated into the (pentachlorophenyl)lithium (**2**) solution, which immediately turned bright red and intensified as the reaction mixture was stirred an additional 2 h at −70 °C and then warmed to room temperature. After stirring 12 h at room temperature, saturated NH$_4$Cl (50 mL) was added, the solution was rotoconcentrated, and the residue was extracted several times with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extracts were combined, washed with water, and dried (Na$_2$SO$_4$). The solvent was rotoevaporated, and the crude mixture was separated by chromatography using Merck silica gel 60 (230–400 mesh) (eluants: hexanes, which gave 1,2,4,5-tetrachlorobenzene (**8**), followed by 19:1 hexanes:acetone, which afforded nitrile **7**, and then acetone, which supplied alkene **9**. The isolated yields of **7**–**9** are shown in Table 1, whereas the mp, elemental analyses, and spectral data for **7** and **9** are given below.

α-Phenyl-α-(2,3,5,6-tetrachlorophenyl)acetonitrile (7a): colorless solid; mp 128–128.5 °C; IR (CHCl$_3$) 2245 cm^{-1} (CN); ^{1}H NMR (CDCl$_3$) δ 6.23 (s, 1 H, CHCN), 7.3 (s, 5 H), 7.68 (s, 1 H, 4-H-C$_6$Cl$_4$). Anal. Calcd for C$_{14}$H$_7$NCl$_4$: C, 50.49, H, 2.14; N, 4.24. Found: C, 50.67; H, 2.10 N, 4.34.

α-(3-Methoxyphenyl)-α-(2,3,5,6-tetrachlorophenyl)acetonitrile (7b): colorless solid; mp 130–131 °C; IR (CHCl$_3$) 2246 cm^{-1} (CN); ^{1}H NMR (CDCl$_3$) δ 3.79 (s, 3 H), 6.28 (s, 1 H), 6.82 (s, 2 H), 6.9 (s, 1 H), 7.3 (t, 1 H), 7.67 (s, 1 H, 4-H-C$_6$Cl$_4$). ^{13}C NMR (CDCl$_3$) δ 39.48, 55.40, 113.11, 116.06, 118.83, 119.47, 130.10, 131.47, 132.88, 133.05, 133.26, 134.50, 160.03.

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[16] Makosza, M.; Serafinowa, B.; Gajos, I. *Roczniki Chem.* **1969**, *43*, 671. (*Chem. Abstr.* **1969**, *71*, 101498).

[17] Banfield, J. E. *J. Chem. Soc.* **1960**, 456.

[18] Molloy, B. M., U.S. Patent 3880927, 1975; *Chem. Abstr.* **1975**, *83*, 27861g.

[19] Haiduc, I.; Gilman, H. *Rev. Roum. Chem.* **1971**, *16*, 907.

[20] Gilman, H.; Jones, R. G. *Org. React.* **1951**, *6*, 339.

[21] We initially thought that nitriles **7** were formed by a lithium–chlorine exchange between **4** and **2** followed by chlorine–lithium exchange of the resulting α-chloro-α-arylacetonitriles **13** and dilithium derivative **12**. Gilman had suggested previously such a mechanism to account for the formation of (trimethylsilyl)-2,3,4,5,6-pentachlorobenzene from the reaction of hexachlorobenzene and (trimethylsilyl)lithium at −70 °C. See: Fearon, F. W. G.; Gilman, H. *J. Organometal. Chem.* **1968**, 73.

[22] Nucleophilic substitution reactions of hexachlorobenzene generally require temperatures above those used in this study. See, for example, Rocklin, A. L. *J. Org. Chem.* **1956**, *21*, 1478 and Kulka, M. *Ibid.* **1959**, *24*, 235. Thus, the usual nucleophilic aromatic substitution mechanism for the facile formation of **7** is unlikely since the transition state leading to the Meisenheimer complex intermediate would be expected to be destabilized by the 4-lithio group.

[23] Ballester, M.; Olivelia, S. *Polychloro-aromatic Compounds*; Suschitzky, H., Ed.; Plenum: New York, 1974; pp 24–27.

Anal. Calcd for $C_{15}H_9NCl_4$: 50.00; H, 2.52; N, 3.89. Found: C, 50.14; H, 2.54; N, 3.85.

α-(4-Methoxyphenyl)-α-(2,3,5,6-tetrachlorophenyl)acetonitrile (7c): colorless solid; mp 140−141 °C; IR ($CHCl_3$) 2248 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) 3.79 (s, 3 H), 6.28 (s, 1 H), 6.86 (d, J = 5.8 Hz, 2 H), 7.23 (d, J = 5.8 Hz, 2 H), 7.67 (s, 1 H, 4-H-C_6Cl_4). Anal. Calcd for $C_{15}H_9NCl_4$: C, 50.00; H, 2.52; N, 3.89. Found: C, 50.11; H, 2.42; N, 3.94.

α-(3,4-Dimethoxyphenyl)-α-(2,3,5,6-tetrachlorophenyl)acetonitrile (7d): colorless solid; mp 148−149 °C; IR ($CHCl_3$) 2245 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 6H), 6.27 (s, 1 H), 6.77 (s, 1 H), 6.78 (d, J = 5.0 Hz, 1 H), 6.87 (d, J = 5.0 Hz, 1 H), 7.67 (s, 1 H, 4-H-C_6Cl_4). Anal. Calcd for $C_{16}H_{11}NCl_4$: C, 49.14; H, 2.83; N, 3.58. Found: C, 49.05; H, 2.71; N, 3.65.

α-[3,4-(Methylenedioxy)phenyl]-α-(2,3,5,6-tetrachlorophenyl)acetonitrile (7e): colorless solid; mp 145−146 °C; IR ($CHCl_3$) 2246 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 5.95 (s, 2H), 6.22 (s, 1 H), 6.74 (s, 1 H), 6.79 (s, 2 H), 7.67 (s, 1 H, 4-H-C_6Cl_4). Anal. Calcd for $C_{15}H_7NCl_4$: C, 48.13; H, 1.89; N, 3.74. Found: C, 48.21; H, 1.97; N, 3.70.

α-(1-Naphthyl)-α-(2,3,5,6-tetrachlorophenyl)acetonitrile (7f): colorless solid; mp 140−142 °C; IR ($CHCl_3$) 2246 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 6.72 (s, 1 H), 7.45 (d, J = 5.1 Hz, 2 H), 7.50−7.62 (m, 2 H), 7.82−7.9 (m, 3 H), 7.74 (s, 1 H, 4-H-C_6Cl_4). Anal. Calcd for $C_{18}H_{10}NCl_4$: C, 56.84; H, 2.38; N, 3.68. Found: C, 56.97; H, 2.41; N, 3.78.

α-(2-Thiophene-yl)-α-(2,3,5,6-tetrachlorophenyl)acetonitrile (7g): colorless solid; mp 105−106 °C; IR ($CHCl_3$) 2250 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 6.40 (s, 1 H), 6.98 (d, J = 5.4 Hz, 1 H), 6.98 (d, J = 5.1 Hz), 1 H), 7.3 (dd, J = 5.1 and 5.4 Hz, 1 H), 7.67 (s, 1 H, 4-H-C_6Cl_4). Anal. Calcd for $C_{12}H_5NSCl_4$: C, 42.85; H, 1.50; N, 4.17. Found: C, 42.97; H, 1.57; N, 4.23.

α-(3-Thiophene-yl)-α-(2,3,5,6-tetrachlorophenyl)acetonitrile (7h): colorless solid; mp 146−147 °C; IR ($CHCl_3$) 2246 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 6.24 (s, 1 H), 7.43 (dd, J = 5.1 Hz, 3.0 Hz, 2 H), 7.73 (dd, J = 5.1 Hz, 1.6 Hz, 2 H), 8.06 (dd, J = 3.0 Hz, 1.6 Hz, 2 H), 7.67 (s, 1 H, 4-H-C_6Cl_4). ^{13}C NMR ($CDCl_3$) δ 35.93, 116.27, 123. Anal. Calcd for $C_{12}H_5NSCl_4$: C, 42.85; H, 1.50; N, 4.17. Found: C, 42.99; H, 1.57; N, 4.22.

α-(3-Tolyl)-α-(2,3,5,6-tetrachlorophenyl)acetonitrile (7i): colorless solid; mp 128−129 °C; IR ($CHCl_3$) 2247 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3 H), 6.30 (s, 1 H), 7.11 (s, 1 H), 7.14−7.24 (m, 3 H), 7.68 (1 H, 4-H-C_6Cl_4). Anal. Calcd for $C_{15}H_{10}NCl_4$: C, 52.32; H, 2.63; N, 4.07. Found: C, 52.38; H, 2.63; N, 4.12.

α-(4-Tolyl)-α-(2,3,5,6-tetrachlorophenyl)acetonitrile (7j): colorless solid; mp 152−153 °C; IR ($CHCl_3$) 2246 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3 H), 6.30 (s, 1 H), 7.19 (s, 4 H), 7.67 (s, 1 H, 4-H-C_6Cl_4). Anal. Calcd for $C_{15}H_8NCl_5$: C, 52.32; H, 2.63; N, 4.07. Found: C, 52.39; H, 2.60; N, 4.18.

1,2-Dicyano-1,2-diphenylethylene (9a): colorless solid; mp 161−162 °C (lit.[18] 160 °C); ^{13}C NMR ($CHCl_3$) δ 116.61, 125.58, 128.65, 129.25, 131.64, 131.98.

1,2-Dicyano-1,2-bis(3-methoxyphenyl)ethylene (9c): colorless solid; mp 212−213 °C; ^{1}H NMR ($CHCl_3$) δ 3.86 (s, 6 H), 7.24 7.43 (m, 6 H), 7.39 (s, 2 H). Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.92; H, 5.18; N, 10.17.

1,2-Dicyano-1,2-bis(4-methoxyphenyl)ethylene (9c): colorless solid; mp 191−192 °C; ^{1}H NMR ($CHCl_3$) δ 3.86 (s, 6 H), 6.99 (d, J = 8.8 Hz, 4 H), 7.78 (d, J = 8.8 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 55.53, 114.56, 117.25, 122.68, 124.60, 130.40, 161.99. Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.71; H, 5.11; N, 10.26.

1,2-Dicyano-1,2-bis[3,4-(methylenedioxy)phenyl]ethylene (9e): colorless solid; mp 226−228 °C; ^{1}H NMR ($CDCl_3$) δ 6.06 (s, 4 H), 6.90 (d, J = 6.9 Hz, 2 H), 7.26 (bs, 2 H), 7.26−7.34 (m, 2 H). Anal. Calcd for $C_{12}H_6N_2S_2$: C, 59.48; H, 2.50; N, 11.56. Found: C, 59.60; H, 2.55; N, 11.63. Calcd for $C_{18}H_{10}N_2O_4$: C, 67.93; H, 3.17; N, 8.80. Found: C, 67.79; H, 3.15; N, 8.83.

1,2-Dicyano-1,2-di-(3-thienyl)ethylene (9h): colorless solid; mp 128.5−129.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.43 (dd, J = 5.1 Hz, 3.0 Hz, 2 H), 7.73 (dd, J = 5.1 Hz, 1.6 Hz, 2 H), 8.06 (dd, J = 3.0 Hz, 1.6 Hz, 2 H). Calcd for $C_{12}H_6N_2S_2$: C, 59.48; H, 2.50; N, 11.56. Found: C, 59.60; H, 2.55; N, 11.63.

General Procedure for the Reaction of Ether Suspensions of Hexachlorobenzene (1) and α-Lithio-α-arylacetonitriles 4. An ether suspension of the lithiated nitrile **4** (11 mmol), prepared in the same manner as described in the general procedure for the reaction of **2**, was cannulated into an ether suspension of **1** at −70 °C. The resulting suspension was allowed to warm to room temperature during which (*ca.* −15 °C to room temperature) the suspension gradually dissolved to give a deep red solution, from which a bright scarlet precipitate gradually formed upon further warming to room temperature and stirring overnight. The mixture was then worked up in the same manner described for the reaction of **2** and **4**. The isolated yields of **10** are shown in Table 1 (entries 11−20), whereas their mp, elemental analyses, and spectral data are given below.

α-Phenyl-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile (10a): colorless solid; mp 141−142 °C; IR ($CHCl_3$) 2246 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 6.23 (s, 1 H, CHCN), 7.3 (s, 5 H). Anal. Calcd for $C_{14}H_6NCl_5$: C, 46.01; H, 1.65; N, 3.83. Found: C, 46.20; H, 1.59; N, 3.98.

α-(3-Methoxyphenyl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile (10b): colorless solid; mp 155−156 °C; IR ($CHCl_3$) 2246 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3 H), 6.28 (s, 1 H, CHCN), 6.82 (s, 2 H), 6.9 (s, 1 H), 7.3 (t, 1 H), 7.67 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 3.79 40.20, 55.91, 113.58, 113.71, 116.40, 119.30, 130.66, 132.79, 133.39, 133.73, 134.07, 135.57, 160.58. Anal. Calcd for $C_{15}H_8NCl_5$: C, 45.55; H, 2.04; N, 3.54. Found: C, 45.67; H, 2.08; N, 3.50.

α-(4-Methoxyphenyl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile (10c): colorless solid; mp 188−190 °C; IR ($CHCl_3$) 2248 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 3.79 (s, 3 H), 6.28 (s, 1 H, CHCN), 6.86 (d, J = 5.8 Hz, 2 H), 7.23 (d, J = 5.8 Hz, 2 H), 7.67 (s, 1 H). Anal. Calcd for $C_{15}H_8NOCl_5$: C, 45.55; H, 2.04; N, 3.54. Found: C, 45.61; H, 2.01; N, 3.59.

α-(3,4-Dimethoxyphenyl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile (10d): colorless solid; mp 132−134 °C; IR ($CHCl_3$) 2249 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 3.84 (s, 6H), 6.27 (s, 1 H, CHCN), 6.77 (s, 1 H), 6.78 (d, J = 5.0 Hz, 1 H), 6.87 (d, J = 5.0 Hz, 1 H), 7.67 (s, 1 H). Anal. Calcd for $C_{16}H_{10}NO_2Cl_5$; C, 46.93; H, 2.46; N, 3.42. Found: C, 46.05; H, 2.36; N, 3.47.

α-[3,4-(Methylenedioxy)phenyl]-α-(2,3,4,5,6-pentachlorophenyl)acetontrile (10e): colorless solid; mp 153−154 °C; IR ($CHCl_3$) 2249 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 3.74 (3.70), 5.95 (s, 2 H), 6.22 (s, 1 H, CHCN), 6.74 (s, 1 H), 6.79 (s, 2 H), 7.67 (s, 1 H). Anal. Calcd for $C_{15}H_6NO_2Cl_5$: C, 44.00; H, 1.48; N, 3.42. Found: C, 44.13; H, 1.42; N, 3.48.

α-(1-Naphthyl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile (10f): colorless solid; mp 170−171 °C; IR ($CHCl_3$) 2250 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 3.68 (3.78) 6.72 (s, 1 H), 7.45 (d, J = 5.1 Hz, 2 H), 7.50−7.62 (m, 2 H), 7.82−7.9 (m, 3 H), 7.74 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 38.54, 116.31, 122.12, 124.94, 125.79, 126.26, 127.16, 127.37, 129.38, 130.12, 130.15, 131.64, 133.43, 133.77, 134.07, 135.05. Anal. Calcd for $C_{18}H_8NCl_5$: C, 52.03; H, 1.94; N, 3.37. Found: C, 52.18; H, 1.99; N, 3.45.

α-(2-Thiophene-yl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile (10g): colorless solid; mp 155−156 °C; IR ($CHCl_3$) 2247 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 6.40 (s, 1 H, CHCN), 6.98 (d, J = 5.4 Hz, 1 H), 6.98 (d, J = 5.1 Hz), 1 H), 7.3 (dd, J = 5.1 and 5.4 Hz, 1 H), 7.67 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 35.47, 114.82, 125.62, 126.43, 126.73, 131.08, 132.45, 132.66, 132.92, 134.59. Anal. Calcd for $C_{12}H_4NSCl_5$: C, 38.80; H, 1.09; N, 3.77. Found: C, 38.91; H, 1.12; N, 3.71.

α-(3-Thiophene-yl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile (10h): colorless solid; mp 150−151 °C; IR ($CHCl_3$) 2246 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 6.24 (s, 1 H, CHCN), 6.90 (d, J = 5.1 Hz, 1 H), 7.29 (d, J = 5.1 Hz, 1 H), 7.3 (s, 1 H), 7.67 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 36.15, 116.14, 123.49, 125.83, 127.37, 131.21, 133.18, 133.26, 134.97. Anal. Calcd for $C_{12}H_4NSCl_5$: C, 38.80; H, 1.09; N, 3.77. Found: C, 38.81; H, 1.14; N, 3.83.

α-(3-Tolyl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile (10i): colorless solid; mp 146−147 °C; IR ($CHCl_3$) 2246 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3 H), 6.30 (s, 1 H, CHCN), 7.11 (s, 1 H), 7.14–7.24 (m, 3 H), 7.68 (1 H). Anal. Calcd for $C_{15}H_8NCl_5$: C, 47.47; H, 2.12; N, 3.69. Found: C, 52.39; H, 2.60; N, 4.18.

α-(4-Tolyl)-α-(2,3,4,5,6-pentachlorophenyl)acetonitrile (10j): colorless solid; mp 165–166 °C; IR ($CHCl_3$) 2246 cm^{-1} (CN); ^1H NMR ($CDCl_3$) δ 2.34 (s, 3 H), 6.30 (s, 1 H, CHCN), 7.19 (s, 4 H), 7.67 (s, 1 H). Anal. Calcd for $C_{15}H_8NCl_5$: C, 47.47; H, 2.12; N, 3.69. Found: C, 47.39; H, 2.10; N, 3.76.

Reaction of α-Halo-α-phenylacetonitriles 4a–j with 1,4-Dilithio-2,3,5,6-tetrachlorobenzene (14). n-Butyllithium (20 mmol, 8 mL of 2.5 M solution) was added dropwise to an ether suspension of **1** ((2.82 g, 10 mmol) at −70 °C, and the resulting solution was stirred for 2 h at −70 °C during which time a clear light brown solution was obtained. α-Chloro-α-(4-methoxyphenyl)acetonitrile (10 mol, 1.81 g) was then added, and the resulting solution was treated similarly as that described for the reaction of **2** and **4** to yield 0.45 g (38%) of 1,2-bis(4-methoxyphenyl)ethylene derivative **9c** and 0.61 g (28%) of tetrachlorobenzene **8**. α-Bromo-α-(4-methoxyphenyl)acetonitrile (10 mol, 2.26 g) treated similarly gave 0.72 g (50%) of **9a** and 0.91 g (42%) of **8**.

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