Hz, 1 H), 0.93 (d, J = 6.4 Hz, 3 H); MS, m/e 141 (17), 123 (19), 112 (41), 111 (39), 97 (61), 95 (28), 82 (34), 70 (26), 69 (89), 55 (100), 41 (75). Anal. Calcd for $C_{10}H_{17}O_2F$: C, 63.79; H, 9.11. Found (cis and trans mixture): C, 63.98; H, 9.10.

Diolide Formation. General Experimental Procedure. To HCl gas in solution (5%, w/w) in methylene chloride (5 mL) was added lactone (*E*)-**4fI** (0.8 mmol). After 30 min, the solvent was removed and the residue purified by liquid chromatography on silica gel (CH_2Cl_2/CH_3COOEt, 90/10–50/50). Diolide **6fI** (R_1 = R_3 = H, R_2 = Me; Scheme V): 70% yield; MS (chemical ionization, NH_3), m/e 326 (M^+ + 18, 11), 309 (100), 208 (19), 190 (40), 155 (37). The main spectroscopic characteristics of diolides **6** prepared are reported in Table V. The other signals are similar to those of the monomeric lactones.

Acknowledgment. We are grateful to Dr. Ottinger and Professor Reisse for the NOE determination and Professor Eliel for a careful reading of the manuscript.

Displacement of Halogen of 2-Halogeno-Substituted Benzonitriles with Carbanions. Preparation of (2-Cyanoaryl)arylacetonitriles

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(2-Cyanoaryl)arylacetonitriles are obtained by displacement of halogen of 2-halobenzonitriles with phenylacetonitrile anions. The method also applies to a number of heteroaromatics with ortho-situated halogen and cyano groups and to heteroarylacetonitrile anions. The anions were generated by using potassium *tert*-butoxide or potassium carbonate. Calculated electron densities of the electrophilic centers reflect the reactivity in the displacement reaction. The calculations indicate that the potassium ion complexes with the cyano group of the 2-halobenzonitriles in nonpolar solvents, thus promoting competitive addition of the anion to the cyano group. Carbanions derived from acids with pK_a ca. 19–23 similarly displaced the halogen of 2-halobenzonitriles.

(2-Cyanophenyl)phenylacetonitriles **3** are useful intermediates for the construction of five- and six-membered rings as described in the following paper. A conceivable route to (2-cyanophenyl)phenylacetonitriles involves treatment of (2-cyanophenyl)phenylhalomethanes with cyanide ions. Of these, only the parent bromo compound has been described.[1] It was prepared by treatment of (2-cyanophenyl)phenylmethane with bromine, conditions that are not compatible with the presence of alkyl groups or electron-donating substituents at the aromatic rings. Therefore, we attempted to prepare (2-cyanophenyl)-phenylchloromethanes by treatment of (2-cyanophenyl-phenyl)hydroxymethanes **5**, available through sodium borohydride reduction of benzophenones, with thionyl chloride. However, the cyano group takes part in the reaction, giving rise to iminolactones, which hydrolyze during workup to lactones **8**, which were isolated in good yields.[1,2]

Another approach to (2-cyanophenyl)phenylacetonitriles **3** is displacement of activated aromatic halogen with the anion of (2-cyanophenyl)acetonitrile (**6**, R = H) (Scheme I). Early attempts to generate this anion and to alkylate it failed since the anion rather adds to unchanged (2-cyanophenyl)acetonitrile.[3] If, however, the anion is generated by using potassium hydroxide in pyridine, it can displace the halogen of nitro-activated halobenzenes **7**.[4] The restrictions of this approach are set by the limited availability of the (2-cyanophenyl)acetonitrile (**6**) and the substituted nitro-activated halobenzenes. The resulting nitro-substituted (2-cyanophenyl)phenylacetonitriles do not undergo further alkylation, the basis for many useful applications of (2-cyanophenyl)phenylacetonitriles.[5] These limitations have been overcome by an approach in which the halogen of 2-halobenzonitriles **1** is displaced by anions from phenylacetonitrile. Although examples of nitro, ester, or cyano group activation of halogen-substituted aromatic rings toward addition of N, O, and S nucleophiles at the position occupied by halogen are abundant,[6] activation by the cyano group toward addition of carbon nucleophiles has only been observed in polycyanochlorobenzenes. Thus 1,4-dichloro-2,3,5,6-tetracyanobenzene and 1,3,5-trichloro-2,4,6-tricyanobenzene both react with carbanions derived from diethyl malonate, malononitrile, or ethyl acetoacetate.[7,8]

The present study reveals that the chlorine of 2-chlorobenzonitrile can be displaced by stabilized benzylic carbanions, notably the phenylacetonitrile anion. The reaction was performed by mixing a solution of the 2-chlorobenzonitrile **1** and the phenylacetonitrile **2** with 2 equiv of a strong base, the second equivalent being required to deprotonate the product (**3**). The reaction is sensitive to the nature of the base, the solvent, the leaving group, the substituents at the rings, and to the kind of rings. In most cases, potassium *tert*-butoxide in dimethylformamide and chlorine serve best as base, solvent, and leaving group, respectively.

Neutral substituents at position 3 of the 2-halobenzonitriles do not influence the reactivity toward addition of nucleophiles at the position occupied by halogen. Thus 2,3-dichlorobenzonitrile reacts smoothly (Table II, entry 2). Electron-donating groups at C-3 and C-5 lead to deactivation. Thus conversion of 2-chloro-5-methoxy-

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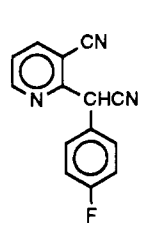
Table I. Preparation of 2-Halogeno-Substituted Benzonitriles and Heteroaryl Nitriles

2-halogeno-substituted benzonitrile 1 or heteroaryl nitrile			recrystllztn[b]		yield[c]
hal	R	method[a]	medium	mp, °C	(overall %)
F	4-Cl	B	HEPT	57–58	68
F	4-Br	A	HEPT	71–73	63
Cl	4-OMe	C	DIPE	70–73	89
Cl	5-OMe	A	DIPE	88–91	49
F	5-OMe	D	DIPE	82–84	51
2-Cl-3-CN-thiophene		B		oil	71
1-$PhCH_2$-4-CN-5-Cl-1,2,3-triazole		E		oil	42

[a] A: The corresponding disubstituted aniline was diazotized and the diazonium ion treated with cuprous cyanide.[15] B: The corresponding disubstituted aromatic acid was treated with hydroxylamine and then with phosphorus tribromide in toluene.[16] C: 2-Chloro-4-nitrobenzonitrile was treated with sodium hydroxide in methanol. D: Sodium 3-chloro-4-fluorophenolate was methylated with dimethyl sulfate in methanol solution and the product heated to reflux for 20 h with cuprous cyanide in *N*-methylpyrrolidone. E: 1-Benzyl-4-(methoxycarbonyl)-5-chloro-1,2,3-triazole[17] was heated with hydroxylamine and then with phosphorus tribromide in toluene.[16] [b] HEPT = *n*-heptane; DIPE = diisopropyl ether. [c] Elementary analyses (C, H, N) of all compounds were within 0.3% of theory.

Table II. Reaction of 2-Halogeno-Substituted Benzonitriles or Heteroaryl Nitriles with Phenyl- or Heteroarylacetonitriles



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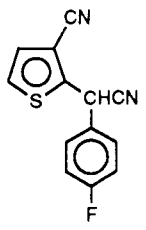

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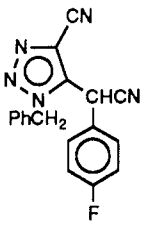

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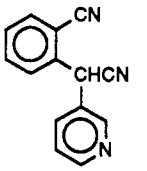

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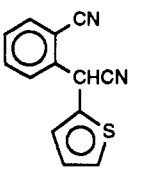

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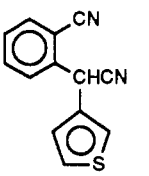

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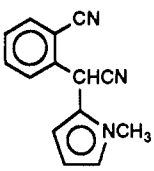

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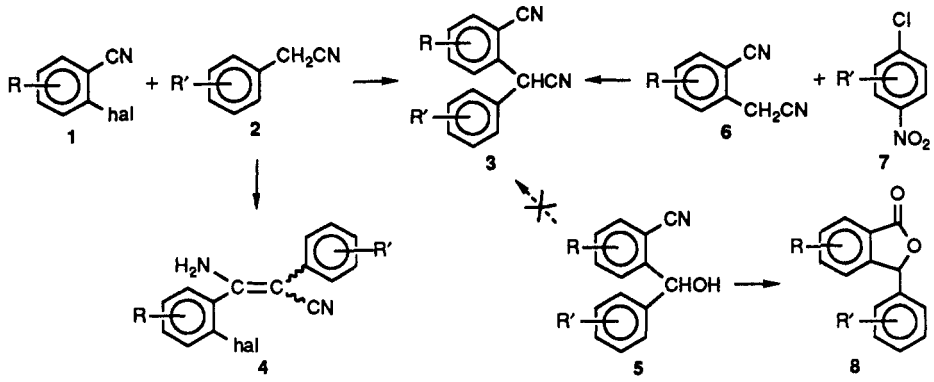
entry	2-halogeno-substituted benzonitrile 1 or heteroaryl nitrile: hal	R	arylacetonitrile 2: R′	base and solvent[a]: A	react temp,[b] °C	time, h	product	mp, °C	yield,[c] %
1	Cl	H	H	A	20	1	3	85–87	87
2	Cl	3-Cl	4-F	A	20	1	3	90–91	73
3	Cl	4-Cl	H	A	20	1	*d*		*d*
4	F	4-Cl	4-F	A	20	1	3	96–98	77
5	F	4-Br	4-F	A	15	1	3	127–129	78
6	Cl	4-OMe	H	A	20	1	3	80–81	79
7	Cl	5-CF_3	4-F	A	20	1	3	oil	79
8	Cl	5-Cl	4-F	A	20	1	3	72–73	82
9	Cl	5-NO_2	4-F	B	80	3	3	134–136	70
10	Cl	5-OMe	H	A	20	3	*d*		*d*
11	F	5-OMe	H	A	20	3	3	76–78	74
12	Cl	6-Cl	4-F	A	15	1	3	91–92	79
13	Cl	H	2-F	A	20	4	3	75–77	69
14	Cl	H	2-OMe	A	20	4	3	104–105	86
15	Cl	H	3-F	A	20	3	3	76–77	77
16	Cl	H	3-OMe	A	20	2	3	68–69	89
17	Cl	H	4-Me	A	20	1	3	64–66	80
18	Cl	H	4-F	A	20	1	3	87–89	86
19	Cl	H	4-Cl	A	20	3	3	oil	85[e]
20	Cl	H	4-OMe	A	25	1	3	68–69	86
21	Cl	H	4-SMe	A	20	2	3	66–68	66
22	Cl	H	3,4-Cl_2	A	25	4	3	87–88	85
23	Cl	H	3,4-$(OMe)_2$	A	20	1	3	118–120	86
24	2-Cl-3-CN-pyridine		4-F	C	80	12	9	126–128	70
25	2-Cl-3-CN-thiophene		4-F	B	20	10	10	66–68	52
26	1-$PhCH_2$-4-CN-5-Cl-1,2,3-triazole		4-F	C	20	4	11		75[f]
27	Cl	H	3-pyridylacetonitrile	A	20	4	12	85–86	74
28	Cl	H	2-thienylacetonitrile	A	20	1	13		67[g]
29	Cl	H	3-thienylacetonitrile	A	20	1	14	oil	78[h]
30	Cl	H	(*N*-methylpyrrol-2-yl)acetonitrile	A	20	4	15	96–98	66

[a] A: Potassium *tert*-butoxide in dimethylformamide. B: Potassium carbonate in *N*-methylpyrrolidone. C: Potassium carbonate in dimethylformamide. [b] The reaction and workup were performed as described in the Experimental Section. [c] Yield of recrystallized, pure substance with the R and R′ given. The C, H, N elemental analyses of all products except entry 26 and 28 gave values within 0.3% of those calculated. [d] See Table III. [e] After ball-tube distillation (250 °C/1 mmHg, 0.5 h). [f] The yield was calculated from an ^1H NMR spectrum. [g] After ball-tube distillation (200 °C/0.1 mmHg, 0.25 h).

benzonitrile requires heating to 60 °C in 1 h (Table II, entry 10) (see below). No restrictions in the nature of substituents at C-4 and C-6 have been observed when substituted by the nucleophile. In fact, the halogen at C-4 of 2,4-dichlorobenzonitrile was displaced more readily than that at C-2. The reactivity of positions occupied by hal-

Scheme I[a]



[a] R and R′, see Tables I and II.

ogen decreases in the order fluorine, chlorine, bromine. Thus, in 2-fluoro-4-chlorobenzonitrile, fluorine was displaced 9 times faster than chlorine with the phenylacetonitrile anion (Table II, entries 4 and 5). Some heteroaromatic *o*-chloro-substituted nitriles may serve as starting materials. In 2-chloro-3-cyanopyridine and 2-chloro-3-cyanothiophene, the halogen could be displaced with the phenylacetonitrile anion generated in dimethylformamide by using potassium carbonate or cesium carbonate as the base (Table II, entries 24 and 25). 1-Benzyl-4-cyano-5-chloro-1,2,3-triazole, an example of an electron-rich heteroaromatic system, also reacted smoothly under these conditions (Table II, entry 26) but 3-chloro-2-cyanothiophene and 3-chloro-4-cyanothiophene decomposed under the conditions of the reaction.

Electron-attracting or -donating substituents at the 3- or 4-positions of the phenylacetonitrile do not influence the reactivity significantly (Table II, entries 13–23). Bulky and electron-attracting substituents at the 2-position reduce the reactivity. Thus with (2-fluoro- or (2-methoxyphenyl)acetonitrile, full conversion required 4 h (Table II, entry 14). Heteroarylacetonitriles may be employed in the process, as exemplified by the smooth reaction of 3-pyridyl-, 2-thienyl-, 3-thienyl-, and (*N*-methyl-2-pyrrolyl)acetonitrile (Table II, entries 27–30).

Potassium *tert*-butoxide effectively deprotonates the phenylacetonitriles. Weaker bases, such as potassium carbonate, may be used when the halogen to be displaced is further activated. This is the case with 2-halobenzonitriles possessing additional electron-attracting substituents at C-3 or C-5 (Table I, entry 9) or with the 2-chloro cyano heterocycles (Table I, entries 24–26). Dimethylformamide serves well as a solvent. Less polar solvents like dimethoxyethane may also be used but competitive addition of the phenylacetonitrile anion to the aromatic cyano group is observed if the reaction is performed in less polar solvents. In such solvents, however, addition of the phenylacetonitrile anion to the aromatic nitrile group with formation of 1-amino-1-(2-halophenyl)-2-cyano-2-phenylethenes 4 competes with displacement of halogen (Table III). The addition reaction becomes more prominent the lower the π^* and β values of the solvent.[9] Thus, 2-chloro-5-methoxybenzonitrile produced the diaryl-1-amino-2-cyanoethene 4 (hal = Cl, R = 5-OMe, R′ = H) exclusively when chlorobenzene was used as the solvent.

The tendency to undergo the addition reaction increases with decreasing difference between the electron densities of C-2 and the cyano group carbon atom as calculated by

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Table III. Influence of the Solvent upon the Ratio between Displacement of the Halogen at C-2 and Addition to the Cyano Group of 2-Halobenzonitriles when Reacted with the Anion of Phenylacetonitrile

2-halobenzonitrile 1		base and solvent[a]	displacement[b] (%)	addition (%)
hal	R			
Cl	H	DMF	87	0
		DME	55	20
		PhCl	1	69
F	H	DMF	90	0
		PhCl	32	56
Cl	5-OMe	DMF	65	16
		PhCl	0	74
F	5-OMe	DMF	74	2
		PhCl	5	77
Cl	5-CF_3	DMF	79	0
		PhCl	59	26

[a] Potassium *tert*-butoxide was used as the base; DME = dimethoxyethane; DMF = dimethylformamide. Reaction temperature and time are given in Table II. [b] When clean displacement or addition occurred the products were isolated and characterized. Mixtures of products were analyzed by ^{1}H NMR (see Experimental Section).

Table IV. Calculated (AM-1 Method[10]) Relative Electron Densities of C-2 and the Cyano Group Carbon Atom of 2-Halobenzonitriles

2-halobenzonitrile 1		electron density			
		uncomplexed		complexed with K^+ ions	
hal	R	C-2	C≡N	C-2	C≡N
Cl	H	−0.0297	−0.0969	−0.0187	0.0320
F	H	0.1319	−0.0959	0.1433	0.0327
Cl	4-OMe	0.0091	−0.0915	0.0275	0.0419
Cl	5-CF_3	−0.0068	−0.1040	0.0025	0.0212
Cl	5-OMe	−0.0679	−0.0970	−0.0608	0.0314
F	5-OMe	0.0937	−0.0962	0.0998	0.0338
Cl	5-NO_2	0.0017	−0.1076	0.0097	0.0149

the semiempirical AM-1 method. In 2-chlorobenzonitrile this electron density difference is 0.07 eu. This seems to be a borderline value since displacement is the prominent reaction in polar solvents while increasing addition is observed in less polar solvents (Table IV). 2-Fluorobenzonitrile, exhibiting a larger electron density difference (0.23 eu), reacts with displacement to a significant extent, even in nonpolar solvents. 2-Chloro-5-methoxybenzonitrile, exhibiting a smaller electron density difference (0.03 eu), reacts with competitive addition amounting to a minimum of 40% when dimethylformamide was used as the solvent. Again, fluorine substitution leads to an increased electron density difference and 2-fluoro-5-methoxybenzonitrile reacts predominantly with displacement. Electron-at-

tracting substituents at C-5 also lead to an increased electron density difference. Thus, 2-chloro-5-(trifluoromethyl)benzonitrile reacts predominantly with displacement, even in nonpolar solvents. The reason why addition becomes more prominent in nonpolar solvents may be due to enhanced polarity of the aromatic cyano group through coordination of its nitrogen atom with potassium ions. Such coordination is less likely in polar solvents that take over the coordination. This hypothesis is strongly supported by calculations extended to include the potassium ion. AM-1 calculations[10] on the complex between 2-chlorobenzonitrile and potassium ion indicate that the ion is situated in the plane of the benzene ring, close to the C≡N bond axis, and 31 nm from the nitrogen atom. The effect of the potassium ion on the charge distribution of 2-chlorobenzonitrile is shown in Table IV. The major effect of the coordination is a decreased electron density of the cyano group carbon atom, which drops below that of C-2 in 2-chlorobenzonitrile. Accordingly, 2-chlorobenzonitrile reacts chiefly with addition when chlorobenzene is used as the solvent. A brief investigation of the reaction of 2-chlorobenzonitrile with other stabilized carbanions revealed that apparently only carbanions derived from acids with pK_a values in the region ca. 19–23 react by displacement of halogen. Successful displacement reactions were performed with phenylacetonitrile (pK_a 21.9)[11], (phenylthio)acetonitrile (pK_a 20.8),[12] (cyclopentenyl)acetonitrile, and phenyl benzyl sulfone (pK_a 23.4).[11] Methyl phenylacetate (pK_a 22.7)[12] gave a complicated mixture of substitution products as methyl and *tert*-butyl esters. Carbanions derived from acids with pK_a values from 10 to 13 such as malononitrile (pK_a 11.1),[12] *tert*-butyl cyanoacetate (pK_a 13.0),[12] benzoylacetonitrile (pK_a 10.2),[13] and (phenylsulfonyl)acetonitrile (pK_a 12.0)[11] did not react at all, while carbanions derived from acids with pK_a values from 29 to 32 such as the anions of dimethyl sulfone (pK_a 31.1)[11] and methyl phenyl sulfone (pK_a 29.0),[14] generated by using sodium hydride or sodium bis(trimethylsilyl)amide, reacted with addition to the aromatic cyano group of 2-chlorobenzonitrile as seen in the ^1H NMR spectra. The cyano group is a suitable activator of adjacent positions occupied by halogen in the displacement reactions. However, a benzoyl group also effects activation. Thus, the chlorine of 2-chlorobenzophenone was readily displaced by the phenylacetonitrile anion. In contrast, methyl 2-chlorobenzoate reacted with addition of the phenylacetonitrile anion to the carbonyl group.

Experimental Section

General. All deprotonations were performed under nitrogen. ^1H NMR spectra were run at 250 MHz on a Bruker AC-250 instrument; δ are in parts per million downfield from $SiMe_4$ as an internal standard. Mass spectra were recorded on a V.G. Micromass 7070F instrument. Elementary analyses were performed by H. Lundbeck A/S, Copenhagen, Denmark.

***o*-Halogenobenzonitriles of Heteroaryl Nitriles.** 2-Chlorobenzonitrile, 2-fluorobenzonitrile, 2,6-dichlorobenzonitrile, 2-chloro-5-nitrobenzonitrile, 2,3-dichlorobenzonitrile, 2,4-dichlorobenzonitrile, 2,5-dichlorobenzonitrile, and 2-chloro-3-cyanopyridine are commercially available. The remaining *o*-halogenoaryl nitriles were prepared as described in Table I.

Arylacetonitriles 2. All arylacetonitriles were commercially available, except 4-(methylthio)phenylacetonitrile, which was made by treating 4-(methylthio)benzyl alcohol with thionyl chloride in dichloromethane followed by reaction with sodium cyanide in dimethyl sulfoxide.[18] Overall yield 67%, mp 38–40 °C (diisopropyl ether).

Other Starting Materials. 2-Chlorobenzophenone, methyl 2-chlorobenzoate, malononitrile, *tert*-butyl cyanoacetate, (phenylsulfonyl)acetonitrile, dimethyl sulfone, and methyl phenyl sulfone are all commercially available. 4-Fluorobenzyl phenyl sulfone was made by treating 4-fluorobenzyl bromide with sodium phenylsulfinate in tetrahydrofuran.[19] Yield 80%, mp 150–152 °C (ethanol). Benzoylacetonitrile was made by treating benzonitrile with acetonitrile in the presence of sodium hydride, *tert*-butyl alcohol, and diethyl ether followed by acidic hydrolysis.[20]

(2-Cyanophenyl)phenylacetonitrile (3) (General Procedure). A mixture of phenylacetonitrile (**1**, R = H) (5.0 g) and 2-chlorobenzonitrile (**2**, R′ = H) (6.2 g) was added with stirring and cooling in an ice bath to a solution of potassium *tert*-butoxide (10.1 g) in dimethylformamide (40 mL) at such a rate that the temperature was maintained at ca. 25 °C. After stirring for an additional 1 hour, saturated aqueous ammonium chloride (200 mL) was added. Extraction with ether (2 × 50 mL) and removal of the ether gave 9.15 g (98%) of (2-cyanophenyl)phenylacetonitrile (**3**, R = R′ = H), mp 85–87 °C (ethanol). Anal. Calcd for $C_{15}H_{10}N_2$: C, 82.55; H, 4.65; N, 12.85. Found: C, 82.5; H, 4.65; N, 12.8. δ_H ($CDCl_3$): 7.75–7.65 (3 H, m, Ar), 7.46–7.31 (6 H, m, Ar), 5.57 (s, 1 H, CH).

***o*-Chloro Cyano Heteroaromatics.** A mixture of 2-chloro-3-cyanopyridine (10 g), 4-fluorophenylacetonitrile (**2**, R′ = 4-F) (10.7 g), potassium carbonate (25 g), tetrabutylammonium hydrogen sulfate (2.5 g), and dimethylformamide (100 mL) was stirred at 80 °C for 18 h. Addition of saturated aqueous ammonium chloride (300 mL), extraction with ethyl acetate (2 × 50 mL), and removal of the ethyl acetate gave 12.0 g (70%) of 2-(3-cyanopyridyl)-4-fluorophenylacetonitrile (**9**), mp 126–128 °C (ethanol). Anal. Calcd for $C_{14}H_8FN_3$: C, 70.85; H, 3.4; N, 17.7. Found: C, 70.45; H, 3.35; N, 17.65.

Competitive Displacement and Addition by Reaction of the Compounds 2 with the Anion of Compound 1. The reaction was performed as for the preparation of (2-cyanophenyl)phenylacetonitriles **3** using the conditions given in Table II. After workup, removal of the ether gave the crude product, which was analyzed by ^1H NMR. The displacement products **3** exhibit a CH signal at 5.5–5.6 ppm, the addition product **4** (*Z* and *E* form) NH_2 signals at 4.8–5.1 ppm, and the starting material **2** a CH_2 signal at 3.7–3.8 ppm.

For characterization of the addition products, crude 1-amino-1-(2-chlorophenyl)-2-cyano-2-(4-fluorophenyl)ethylene (**4**, hal = Cl, R = H, R′ = 4-F) was flash chromatographed[21] (trichloroethane) to give 17% of the *Z* isomer (R_f 0.30), mp 143–145 °C. Anal. Calcd for $C_{15}H_{10}ClFN_2$: C, 66.05; H, 3.7; N, 10.25. Found: C, 65.85; H, 3.6; N, 9.95. δ_H ($CDCl_3$): 7.00–7.60 (8 H, m, Ar), 4.73 br (2 H, s, NH_2). The next fraction contained 71% of the *E* isomer (R_f 0.23), mp 156–157 °C (diisopropyl ether). (Found: C, 65.9; H, 3.6; N, 9.95). δ_H ($CDCl_3$): 6.70–7.50 (8 H, m, Ar), 5.00 br (2 H, s, NH_2). The *Z* isomer isomerizes slowly to the *E* isomer upon heating to 100 °C in toluene. The *E* isomer is stable under these conditions.

Competitive Displacement of 2- and 4-Halogen of Compound 1. Phenylacetonitrile (**2**; R′ = H) and 2,4-dichlorobenzonitrile (**1**, hal = Cl, R = 4-Cl) were reacted as above to give a crude product, which according to ^1H NMR contained a 3.8:1 mixture of (3-chloro-4-cyanophenyl)(4-fluorophenyl)acetonitrile and (4-chloro-2-cyanophenyl)phenylacetonitrile (**3**; R = 3-Cl, R′ = H). The products were identified by addition of the pure

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substances to the solution. Pure (3-chloro-4-cyanophenyl)-phenylacetonitrile, mp 85–87 °C, was obtained in 68% yield, replacing 2,4-dichlorobenzonitrile above with 2-chloro-4-nitrobenzonitrile. Anal. Calcd for $C_{15}H_9N_2Cl$: C, 71.3; H, 3.6; N 11.1. Found: C, 71.45; H, 3.55; N, 11.1.

Reactions of 2-Chlorobenzonitrile (1) with Activated Methylene Compounds. 4-Fluorobenzyl phenyl sulfone (85 g) was added with stirring to a solution of potassium *tert*-butoxide (84 g) in dimethylformamide (200 mL) at such a rate that the temperature is maintained at 30–35 °C. After stirring for additional 15 min, a solution of 2-chloro-5-(trifluoromethyl)benzonitrile (1; hal = Cl, R = 5-CF_3) (85 g) in dimethylformamide (100 mL) was added at 25–30 °C. Stirring at 60 °C for 4 h, cooling to 20 °C, and workup as described for **3** (R = R′ = H) afforded 121 g (85%) of (2-cyano-4-(trifluoromethyl)phenyl)(4-fluorophenyl)methyl phenyl sulfone, mp 108–109 °C (ethanol). Anal. Calcd for $C_{21}H_{13}F_4NO_2S$: C, 60.15; H, 3.15; N, 3.35. Found: C, 60.3; H, 3.3; N, 3.2. δ_H ($CDCl_3$): 6.90–8.65 (12 H, m, Ar); 5.80 (1 H, s, CH).

Reaction of Methyl 2-Chlorobenzoate with the Anion of (4-Fluorophenyl)acetonitrile. Methyl 2-chlorobenzoate and (4-fluorophenyl)acetonitrile (**2**, R′ = 4-F) were reacted as described for **3** (R = R′ = H) and the mixture worked up as described for **9** to give 60% of 1-hydroxy-1-(2-chlorophenyl)-2-cyano-2-(4-fluorophenyl)ethylene (probably the *E* form), mp 158–160 °C (ethanol). Anal. Calcd for $C_{15}H_9ClFNO$: C, 65.8; H, 3.3; N, 5.1. Found: C, 65.55; H, 3.1; N, 4.9.

Reaction of 2-Chlorobenzophenone with the Anion of Phenylacetonitrile. A solution of phenylacetonitrile (5.0 g) and 2-chlorobenzophenone (10.2 g) in dimethylformamide (20 mL) was added with stirring to a solution of potassium *tert*-butoxide (10.1 g) in dimethylformamide (40 mL). Stirring for 18 h, addition of saturated aqueous ammonium chloride (100 mL), extraction with ether (2 × 50 mL), and removal of the ether gave 12.5 g of crude product. Recrystallization (ethanol) afforded 8.8 g (69%) of (2-benzoylphenyl)phenylacetonitrile, mp 103–105 °C. Anal. Calcd for $C_{21}H_{15}NO$: C, 84.8; H, 5.1; N, 4.7. Found: C, 84.95; H, 5.15; N 4.85. δ_H ($CDCl_3$): 6.75–7.75 (m, 13 H, Ar), 5.83 (1 H, s, CH).

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Registry No. 1 (hal = Cl, R = H), 873-32-5; 1 (hal = Cl, R = H) K^+ complex, 127667-33-8; 1 (hal = Cl, R = 3-Cl), 6574-97-6; 1 (hal = Cl, R = 4-Cl), 6574-98-7; 1 (hal = Cl, R = 5-CF_3), 328-87-0; 1 (hal = Cl, R = 5-CF_3) K^+ complex, 127667-36-1; 1 (hal = Cl, R = 5-Cl), 21663-61-6; 1 (hal = Cl, R = 5-NO_2), 16588-02-6; 1 (hal = Cl, R = 5-NO_2) K^+ complex, 127667-39-4; 1 (hal = Cl, R = 6-Cl), 1194-65-6; 1 (hal = F, R = 4-Cl), 57381-51-8; 1 (hal = F, R = 4-Br), 105942-08-3; 1 (hal = Cl, R = 4-OMe), 127666-99-3; 1 (hal = Cl, R = 4-OMe) K^+ complex, 127667-35-0; 1 (hal = Cl, R = 5-OMe), 127667-00-9; 1 (hal = Cl, R = 5-OMe) K^+ complex, 127667-37-2; 1 (halo = F, R = 5-OMe), 127667-01-0; 1 (hal = F, R = 5-OMe) K^+ complex, 127667-38-3; 1 (hal = F, R = H) K^+ complex, 127667-34-9; **2** (R′ = 2-F), 326-62-5; **2** (R′ = 2-OMe), 7035-03-2; **2** (R′ = 3-F), 501-00-8; **2** (R′ = 3-OMe), 19924-43-7; **2** (R′ = 4-Me), 2947-61-7; **2** (R′ = 4-Cl), 140-53-4; **2** (R′ = 4-OMe), 104-47-2; **2** (R′ = 4-SMe), 38746-92-8; **2** (R′ = 3,4-Cl_2), 3218-49-3; **2** (R′ = 3,4-$(OMe)_2$), 93-17-4; **2** (R′ = H), 140-29-4; **2** (R′ = 4-F), 459-22-3; **3** (R = R′ = H), 127667-03-2; **3** (R = 3-Cl, R′ = 4-F), 127667-04-3; **3** (R = 4-Cl, R′ = 4-F), 127667-05-4; **3** (R = 4-Br, R′ = 4-F), 127667-06-5; **3** (R = 4-OMe, R′ = H), 127667-07-6; **3** (R = 5-CF_3, R′ = 4-F), 127667-08-7; **3** (R = 5-Cl, R′ = 4-F), 127667-09-8; **3** (R = 5-NO_2, R′ = 4-F), 127667-10-1; **3** (R = 5-OMe, R′ = H), 127667-11-2; **3** (R = 6-Cl, R′ = 4-F), 127667-12-3; **3** (R = H, R′ = 2-F), 127667-13-4; **3** (R = H, R′ = 2-OMe), 127667-14-5; **3** (R = H, R′ = 3-F), 127667-15-6; **3** (R = H, R′ = 3-OMe), 127667-16-7; **3** (R = H, R′ = 4-Me), 127667-17-8; **3** (R = H, R′ = 4-F), 116617-31-3; **3** (R = H, R′ = 4-Cl), 127667-18-9; **3** (R = H, R′ = 4-OMe), 127667-19-0; **3** (R = H, R′ = 4-SMe), 127667-20-3; **3** (R = H, R′ = 3,4-Cl_2), 127667-21-4; **3** (R = H, R′ = 3,4-$(OMe)_2$), 127667-22-5; **9**, 127667-23-6; **10**, 127667-24-7; **11**, 127667-25-8; **12**, 127667-26-9; **13**, 127667-27-0; **14**, 127667-28-1; **15**, 127667-29-2; 4-$FC_6H_4CH_2SO_2Ph$, 78974-45-5; 2-$ClC_6H_4C(O)OMe$, 610-96-8; *E*-2-$ClC_6H_4C(OH)$=$C(CN)C_6H_4$-4-F, 127667-31-6; 2-$ClC_6H_4C(O)Ph$, 5162-03-8; 2-$PhC(O)C_6H_4CH(Ph)C{\equiv}N$, 127667-32-7; 2-Cl-3-CN-pyridine, 6602-54-6; 2-Cl-3-CN-thiophene, 127667-02-1; 1-$PhCH_2$-4-CN-5-Cl-1,2,3-triazole, 103912-97-6; 3-pyridylacetonitrile, 6443-85-2; 2-thienylacetonitrile, 20893-30-5; 3-thienylacetonitrile, 13781-53-8; N-methylpyrrol-2-ylacetonitrile, 24437-41-0; (2-cyano-4-(trifluoromethyl)phenyl)(4-fluorophenyl)methyl phenyl sulfone, 127667-30-5.