(m, 4), 7.2–7.75 (m, 9). **25h**: 4.81 (m, 2), 7.12 (d, 1, J = 8), 7.35–7.74 (m, 5), 7.86 (dd, 1, J = 2, J = 8), 8.20 (d, 1, J = 2). **25i**: 4.00 (s, 4), 4.91 (s, 2), 5.79 (s, 1), 7.25 –7.65 (m, 8), 8.01 (d, 1, J = 2). **25j**:[41e] 5.20 (s, 2), 7.5–7.95 (m, 6), 8.10 (dd, 1, J = 2, J = 8), 8.50 (d, 1, J = 2). **25k**:[41d] 3.30 (s, 3), 5.24 (s, 2), 7.5–7.95 (m, 6), 8.19 (dd, J = 2, J = 9), 8.48 (d, 1, J = 2). **25e**: 5.05 (s, 2), 7.2–8.0 (m, 7), 8.3 (s, 1). **25m**: 1.34 (s, 9), 4.86 (s, 2), 7.25–7.75 (m, 7), 7.92 (d, 1, J = 1.5). **26a**: 3.42 (s, 3), 5.03 (s, 2), 7.3–7.8 (m, 8). **26b**: 5.21 (s, 2), 7.2–7.9 (m, 8). **26c**: 5.42 (s, 2), 7.35–8.2 (m, 8). **26d**: 3.5 (s, 3), 5.08 (s, 2), 6.9–7.1 (m, 1), 7.35–7.8 (m, 7). **26e**: 5.15 (s, 2), 7.3–8.0 (m, 8). **31**: 6.52 (s, 2), 7.3–7.8 (m, 10), 8.45–8.9 (m, 3). **32**: 0.8–1.4 (m, 9), 2.1–2.3 (m, 2), 2.4–2.8 (m, 4), 3.6–3.7 (m, 4), 4.21 (dd, 1, J = 3.5, J = 10.5), 7.54 (d, 2, J = 9), 8.32 (d, 2, J = 9). **33**: 0.8–1.5 (m, 5), 2.0–2.5 (m, 2), 2.9–3.4 (m, 4), 3.6–3.8 (m, 4), 4.22 (dd, 1, J = 4, J = 9), 7.61 (d, 1, J = 9), 7.75 (s, 1), 8.05 (d, 1, J = 9). **34**: 3.0–3.3 (m, 4), 3.6–3.7 (m, 4), 5.52 (s, 1), 7.82 (d, 2, J = 8.5), 8.30 (d, 2, J = 8.5). **35**: 3.60 (s, 3), 7.22 (s, 1), 7.50 (s, 5), 8.43 (d, 1, J = 8), 8.6 (dd, 1, J = 2, J = 8), 8.90 (d, 1, J = 2).

Acknowledgment. This work was supported by Grant MR-I.12.1. We are indebted to Fluka A. G. Buchs for generous gifts of chemicals.

Registry No. **1**, 7205-98-3; **2**, 39542-27-3; **3**, 98-95-3; **4**, 34063-53-1; **5**, 89303-08-2; **6**, 69709-34-8; **7**, 89303-09-3; **8a**, 100-00-5; **8b**, 100-23-2; **8c**, 100-17-4; **8d**, 620-88-2; **8e**, 100-12-9; **8f**, 3282-56-2; **8g**, 2403-53-4; **8h**, 92-93-3; **8i**, 701-57-5; **8j**, 586-78-7; **8k**, 636-98-6; **8l**, 350-46-9; **8m**, 100-25-4; **8n**, 619-72-7; **8o**, 402-54-0; **8p**, 2976-30-9; **8r**, 62-23-7; **9a**, 89303-10-6; **9b**, 89303-11-7; **9c**, 69709-39-3; **9d**, 89303-12-8; **9e**, 89303-13-9; **9f**, 89303-14-0; **9g**, 89303-15-1; **9h**, 69709-40-6; **9i**, 89303-16-2; **9j**, 69709-38-2; **9k**, 89303-17-3; **9l**, 89303-18-4; **9m**, 89303-19-5; **9n**, 89303-20-8; **9o**, 89303-21-9; **9p**, 89303-22-0; **9r**, 89303-23-1; **10a**, 69709-37-1; **11**, 20808-12-2; **12**, 19169-90-5; **13**, 65492-21-9; **14**, 69709-41-7; **15**, 5533-31-3; **16**, 31540-74-6; **17**, 69709-35-9; **18**, 69709-36-0; **19**, 7693-38-1; **20a**, 88-73-3; **20b**, 610-17-3; **20c**, 91-23-6; **20d**, 2216-12-8; **20e**, 88-72-2; **20f**, 384-22-5; **20g**, 528-29-0; **20h**, 1886-57-3; **21a**, 86434-25-5; **21b**, 89303-24-2; **21c**, 89303-25-3; **21d**, 89303-26-4; **21e**, 89303-27-5; **21f**, 89303-28-6; **21g**, 89303-29-7; **22a**, 86434-29-9; **22b**, 89303-30-0; **22c**, 89303-31-1; **22d**, 89303-32-2; **22e**, 89303-33-3; **22f**, 89303-34-4; **23a**, 99-08-1; **23b**, 121-73-3; **23c**, 585-79-5; **23d**, 555-03-3; **23e**, 402-67-5; **23f**, 619-31-8; **23g**, 620-55-3; **23h**, 645-00-1; **23i**, 6952-67-6; **23j**, 619-24-9; **23k**, 2976-32-1; **23l**, 98-46-4; **23m**, 23132-52-7; **23n**, 99-65-0; **24a**, 86434-26-6; **24b**, 89303-35-5; **24c**, 89303-36-6; **24d**, 86434-27-7; **24e**, 86434-28-8; **24f**, 89303-37-7; **24g**, 89303-38-8; **24h**, 89303-39-9; **24i**, 89303-40-2; **24j**, 89303-41-3; **24k**, 89303-42-4; **24l**, 89303-43-5; **24n**, 89303-44-6; **25a**, 86434-30-2; **25b**, 89303-45-7; **25c**, 89303-46-8; **25d**, 86434-31-3; **25e**, 86434-32-4; **25f**, 89303-47-9; **25g**, 89303-48-0; **25h**, 89303-49-1; **25i**, 89303-50-4; **25j**, 89303-51-5; **25k**, 89303-52-6; **25l**, 89303-53-7; **25m**, 89303-54-8; **26a**, 86434-33-5; **26b**, 89303-55-9; **26c**, 89303-56-0; **26d**, 86434-34-6; **26e**, 86434-35-7; **27**, 69083-63-2; **28**, 69083-62-1; **29**, 71376-64-2; **30**, 69083-60-9; **31**, 89303-57-1; **32**, 89303-58-2; **33**, 89303-59-3; **34**, 89303-60-6; **35**, 89303-61-7; sodium benzenesulfinate, 873-55-2; chlorobromomethane, 74-97-5; dibromomethane, 74-95-3.

Vicarious Nucleophilic Substitution of Hydrogen in Nitroarenes with α-Substituted Nitriles and Esters. Direct α-Cyanoalkylation and α-Carbalkoxyalkylation of Nitroarenes[1]

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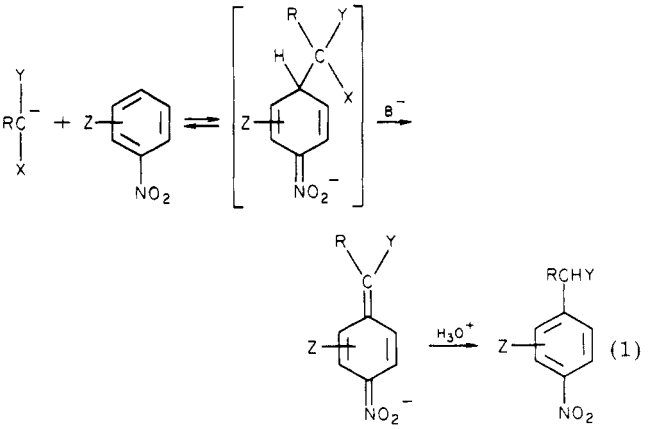
Carbanions generated from alkanenitriles bearing α-chloro, α-OR, or α-SR groups and from aliphatic esters bearing α-SR groups react with mononitroarenes to replace hydrogen atoms of the nitroaromatic ring ortho or para to the nitro group with α-cyanoalkyl or α-carbalkoxyalkyl substituents. The nucleophilic replacement of hydrogen with such carbanions proceeds faster than substitution of halogen ortho or para to the nitro group.

Introduction

In our studies of the vicarious nucleophilic substitution of hydrogen in nitroarenes by carbanions.[2,3] We have shown that a variety of carbanions $RXYC^-$ enter this reaction, which proceeds via fast and reversible addition of the carbanions to nitroarenes, giving the σ complexes, followed by base-induced elimination of HX (eq 1).[4] X is a leaving group and Y a carbanion stabilizaing group. We have demonstrated that acetonitrile derivatives could serve as sources of carbanions for this reaction.[2] Although



there are a few reports of reactions that appear to involve vicarious substitution of hydrogen in aromatic nitro compounds,[5] no systematic study of the reaction has been

(1) Part 110 in the series reactions of organic anions. Part 109: *J. Org. Chem.*, preceding paper in this issue.
(2) Makosza, M.; Winiarski, J. *J. Org. Chem.* **1980**, *45*, 1534.
(3) (a) Goliński, J.; Makosza, M. *Tetrahedron Lett.* **1978**, 3495. (b) Makosza, M.; Goliński, J.; Pankowski, J. *Synthesis* **1983**, 40. (c) Goliński, J.; Makosza, M. *Angew. Chem.* **1982**, *88*, 468. (d) Makosza, M. In "Current Trends in Organic Synthesis"; Nozaki, H., Ed.; Pergamon Press: Oxford, 1983; p 401.
(4) Makosza, M.; Glinka, T. *J. Org. Chem.* **1983**, *48*.

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Table I. Reactions of Nitroarenes with 1a (eq 2)

Z	solvent	total yield,[a] %	o/p
H	NH_3	9.2[b]	3.7[c]
	Me_2SO	46[b]	4.8[c]
2-Cl	NH_3	6	7.5[c]
3-Cl	NH_3	38	5[d,e]
4-Cl	NH_3	75	only o
	Me_2SO	40	only o
	NH_3	75	30[e]
C_4H_4[f]	Me_2SO	62	13[e]

[a] Yields of isolated mixture of isomers. [b] 10-fold molar excess of nitrobenzene. [c] Determined by GC. [d] Only one ortho isomer: 2-Cl-6-$O_2NC_6H_3CH_2CN$ was formed. Another isomer (4-Cl-2-$O_2NC_6H_3CH_2CN$) was not detected. [e] Determined by NMR. [f] 1-Nitronaphthalene.

made. In the preceding paper[1] we reported on α-haloalkyl aryl sulfones and sulfonamides as sources of carbanions for vicarious substitution of hydrogen in nitrobenzenes. We now report on a study of the vicarious substitution of hydrogen in nitroarenes with carbanions derived from aliphatic nitriles and esters bearing halogen, OR, or SR groups in the α position.

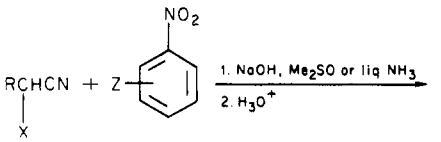
Results and Discussion

Reactions of α-Chloronitriles with Nitroarenes. We have reported the cyanomethylation of 4-chloronitrobenzene and 1-nitranaphthalene with chloroacetonitrile (**1a**) in the presence of sodium hydroxide Me_2SO.[2] Further examples of the reactions of **1a** with nitroarenes in the presence of sodium hydroxide in Me_2SO or liquid ammonia are given in Table I. Chloroacetonitrile undergoes rapid self-condensation in the presence of strong bases. Hence it reacts in vicarious substitution only with active nitroarenes such as halonitrobenzenes and 1-nitronaphthalene. Its reaction with nitrobenzene proceeds slowly and is very sensitive to reaction conditions. Even with a 10-fold excess of nitrobenzene in Me_2SO the yield, a mixture of 2- and 4-nitrophenylacetonitriles, is only 46%. In all reactions of **1a** there is a strong preference for the formation of the ortho over the para isomer, from 4:1 with nitrobenzene to 30:1 with 1-nitronaphthalene.[6] In the reaction of **1a** with 2-chloronitrobenzene, substitution takes place mainly at the ortho′ 6 position. More surprising is that in 3-chloronitrobenzene substitution at the 2 position predominates over that at the 4 position, whereas the 6 isomer is not formed. The assignments of product structures were based on NMR spectra and physical properties of the three isomeric (chloronitrophenyl) acetonitriles: 2-Cl-6-NO_2, 2-Cl-4-NO_2, and 4-Cl-2-NO_2; the last compound was formed in the reaction of 3-chloronitrobenzene with **1b**.

Table II. Reaction of Nitroarenes with 2a and 3a (eq 2)

substrates Z	substrates nitrile	substitution at position	yield,[a] %
H	**2a**	p	34
2-Cl	**2a**	p	38
2-F	**2a**	p	41
4-Cl	**2a**	o	14
H	**3a**	p	60
2-Cl	**3a**	p	51
4-Cl	**3a**	o	13[b]

[a] Yields of isolated compounds. [b] 4-$O_2NC_6H_4CH(CN)$-$CHMe_2$ (yield 14%) was also isolated.



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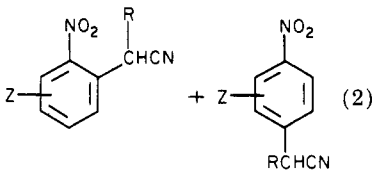


(2)

R = H; **1a**, X = Cl; **1b**, X = PhS; **1c**, X = Me_2NCS_2; **1d**, X = MeS; **1e**, X = PhO
R = Me; **2a**, X = Cl; **2b**, X = PhS
R = $CHMe_2$, **3a**, X = Cl; **3b**, X = PhS
R = Ph; **4e**, X = PhO; **4f**, X = 4-ClC_6H_4O; **4g**, X = 2,4-$Cl_2C_6H_3O$; **4h**, X = MeO

Self-condensation of α-chloroalkanenitriles **2a** and **3a** in the presence of bases is slower than that of **1a**. As a result they usually react with nitroarenes better than **1a**, although the yields of products are still not very high (Table II). In accord with our previous observation that tertiary carbanions stabilized by sulfonyl groups do not replace hydrogen ortho to the nitro group,[1,3a] the tertiary carbanions formed from these nitriles react preferentially at the para position. Nevertheless, in the reaction with 4-chloronitrobenzene, both **2a** and **3a** replace some ortho hydrogen; obviously the cyano group has a smaller steric effect than the sulfonyl group. In the reaction of **3a** with 4-chloronitrobenzene, 2-(4-nitrophenyl)isovaleronitrile is also formed, apparently via the substitution of halogen by **3a** followed by reductive dechlorination of the initial product (Table II).

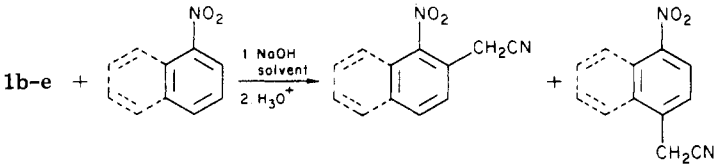
Although the yields reported in Tables I and II are only moderate, they can probably be improved with further study of reaction conditions. Thus the conditions for cyanomethylation of 4-chloronitrobenzene with **1a** were varied to increase the yield of (5-chloro-2-nitrophenyl)-acetonitrile to 75%.

Reactions of α-OR and α-SR Substituted Nitriles. In constrast to halogen, OR and SR substituents are not easily replaced in S_N2 reactions with other nucleophiles, and the nitriles RCHXCN (X = OR, SR) (eq 2) are relatively stable in the presence of strong base. We have reported that **1a** and **4e** react with some nitroarenes to effect vicarious substitution.[2] Further studies have shown that nitriles **1b–d**, **2b**, **3b**, and **4e–h** react with a variety of nitroarenes in the presence of NaOH in Me_2SO to give α-cyanoalkyl derivatives. Yields of products are given in Tables III–V, and physical properties are given in the

(5) Methylation with dimethylsulfoxonium methylide: Traynelis, V. J.; McSweeney, J. V. *J. Org. Chem.* **1966**, *31*, 243. Metzger, H.; König, H.; Seelert, K. *Tetrahedron Lett.* **1964**, 867. Methylation with dimethyl sulfoxide anion: Russell, G. A.; Weiner, S. A. *J. Org. Chem.* **1966**, *31*, 248. Dichloromethylation with (trichloromethyl)lithium: McBee, E. T.; Wesseler, E. P.; Hodgins, T. *J. Org. Chem.* **1971**, *36*, 2907. Carboalkoxy methylation of 2-nitrofuran ring with pyridinium carbobalkoxy methylide: Tanaka, A.; Usui, T. *J. Heterocycl. Chem.* **1979**, *16*, 1409.

(6) We reported earlier[2] that the principal product of the reaction of chloroacetonitrile with 1-nitronaphthalene was the 1,4 isomer and the minor product the 1,2 isomer. This report was in error; it was based on a misinterpretation of the ^1H NMR spectrum and the fact that the principal product on reduction gave an aminonitrile rather than cyclizing to an indole derivative.[21] We have now shown that the principal product is the 1,2 isomer by hydrolyzing it to the known (1-nitro-2-naphthyl)acetic acid (see Experimental Section). In addition, the minor product has been shown to be identical with the nitrile prepared from known (4-nitro-1-naphthyl)acetic acid.[13] The main product upon alkylation with methyl iodide gave the product different from that obtained via the vicarious substitution of hydrogen in 1-nitronaphthalene with 2-thiophenoxypropionitrile (see infrared data). It is well documented that tertiary carboanions replace hydrogen para to the nitro group.[1,3a-d]

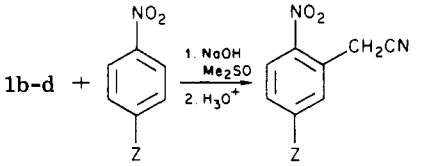
Table III. Reactions of Nitriles 1b-e with Nitrobenzene and 1-Nitronaphthalene



nitrile	solvent	conc of reagents, mol/dm³	molar excess of NaOH	temp, °C	nitrobenzene total yield,[a] %	nitrobenzene o/p[b]	1-nitronaphthalene total yield,[a] %	1-nitronaphthalene o/p[c]
1e	Me_2SO	0.5	5	25	37	7.1	80	13
1c	Me_2SO	0.5	5	25	68	1.4		
1d	Me_2SO	0.5	5	25	43	1.1	88	8
1b	pyridine	0.5	5	25	31	1.9	75	7
1b	Me_2SO	0.5	5	25	80	0.91	94	11
1b	Me_2SO	0.5	5	40	68	0.67		
1b	Me_2SO	0.125	5	40	56	0.17		
1b	Me_2SO	0.125	20	40	62	0.46		

[a] Yields of isolated mixture of isomers. [b] Determined by GC. [c] Determined by ^1H NMR.

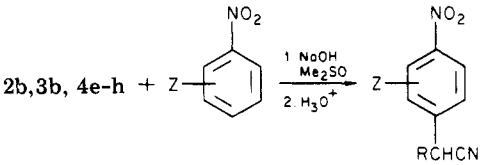
Table IV. Reaction of Nitroarenes with 1b, 1c, 1d



substrates Z	substrates nitrile	yield,[a] %
Cl	1c	71
F	1b	19[b]
MeO	1c	31[c]
EtO	1c	49[c]
MeS	1c	40[c]
MeS	1d	39
PhS	1b	74
t-Bu	1b	58
Ph	1b	74

[a] Yields of isolated compounds. [b] A mixture of products Z = PhS (19%) and 4-$O_2NC_6H_4CH(CN)SPh$ (41%) was formed. [c] A 50% molar excess of 1c was used.

Table V. Reactions of Nitroarenes with 2b, 3b, 4e-h



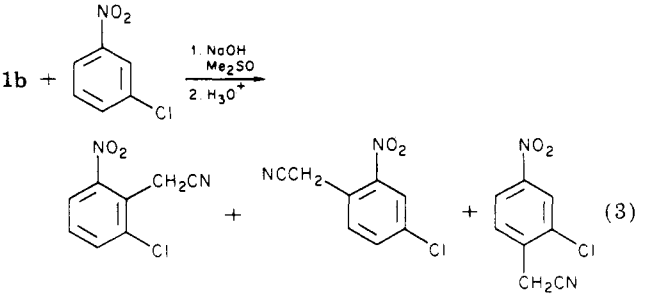
substrates Z	substrates nitrile	yield,[a] %
H	2b	79
2-Cl	2b	72[b]
C_4H_4[c]	2b	71
H	3b	69
3-Cl	3b	63
2-MeO	3b	17
C_4H_4[c]	3b	47
H	4e	42
2-Cl	4e	55
C_4H_4[c]	4e	77
H	4f	59
C_4H_4[c]	4f	81
H	4g	57
C_4H_4[c]	4g	76
H	4h	42
C_4H_4[c]	4h	49

[a] Yields of isolated compounds. [b] A mixture of the products Z = Cl and Z = PhS, ratio ca. 1:1.2 was formed. [c] 1-Nitronaphthalene.

Experimental Section. Structures of the products were confirmed by spectral and elemental analyses. In addition, the reaction product of **4e** with 1-nitronaphthalene was converted into the known 1-(acetylamino)-4-benzoylnaphthalene in order to establish independently the orientation of substitution (see also note 6).

As indicated by the data in Tables III–V, α-cyanoalkylation with carbanions of these nitriles can be applied to a range of mononitroarenes with generally good yields. Acetonitriles **1b–e** can replace hydrogen in positions both ortho and para to the nitro group. The o/p ratios appear to be strongly influenced by the nature of the leaving group and to a smaller extent by the reaction conditions. In reactions of α-substituted acetonitriles with nitrobenzene, the leaving groups can be put in the following order of decreasing o/p ratio: PhO (7.1), Cl (4.8), Me_2NCS_2 (1.4), MeS (1.1), and PhS (0.91). In reactions of 1-nitronaphthalene the o/p ratio is much higher, ranging from 30 to 8, and is less sensitive to the nature of the leaving group. The o/p ratio also depends on the reaction conditions. When cation–carbanion association is strong (e.g., in pyridine rather than Me_2SO, or using higher concentrations of reactants and base in Me_2SO), the ortho orientation is preferred. The complex correlation of the orientation with the structural feactures of the reactants and reaction conditions is being studied further.

Cyanomethylation of 3-chloronitrobenzene with **1b** leads to three isomeric products in a total yield of 92%. The ratio of the isomers compared to that formed from **1a** is shown in eq 3.



(3)

1b, 1	2.1	8.5
1a, 5	0	1

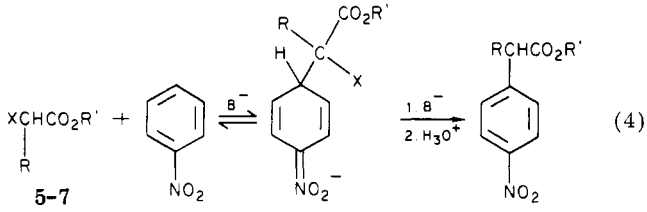
Nitriles **2–4** substitute only the hydrogen para to the nitro group, which is typical for tertiary carbanions. When

the para position is occupied by a substituent, the reaction may not proceed (e.g., **3b** does not react with 4-nitrobiphenyl); however, if the para substituent has nucleofugal character, typical nucleophilic substitution of it takes place. For example, **4h** and 4-chloronitrobenzene form α-methoxy-α-(4-nitrophenyl)phenylacetonitrile.[7] In general, when there are no obstacles to the vicarious substitution of hydrogen, substitution of halogen does not compete. Only in the reaction of 4-fluoronitrobenzene with nitrile **1b** do both substitution of halogen and hydrogen by the carbanion occur.

Since the PhS^- anion produced in the reactions of **1b**, **2b**, and **3b** with nitroarenes is a powerful nucleophile, reactions of these nitriles with *o*- and *p*-halonitrobenzenes give not only the expected products of the substitution of hydrogen but also products of the replacement of halogen by the PhS group (Table IV and V). This replacement can occur via reaction of PhS^- with the starting halonitrobenzene as well as with the products of hydrogen replacement. This complication of the reaction course can be eliminated by the use of nitriles containing the Me_2NCS_2 leaving group (e.g., **1c**). The dithiocarbamate anion produced during this reaction does not replace chlorine in the nitroarene ring: reaction of **1c** with 4-chloronitrobenzene gives (5-chloro-2-nitrophenyl)acetonitrile in a yield of 71%.

α-Cyanobenzylation of nitroarenes does not proceed with α-chlorolphenylacetonitrile because of its rapid base-induced self-condensation to produce dicyanostilbene;[8] accordingly α-(aryloxy) and α-methoxy nitriles **4e–h** are the reagents of choice. On the other hand, their thio analogues do not react with nitroarenes in basic media, perhaps because of the lower nucleophilicity of the corresponding carbanions.

Reactions of Esters of α-Thio Substituted Carboxylic Acids. Reactions of ethyl or *tert*-butyl chloroacetates and ethyl α-chloropropionate with nitroarenes in the presence of NaH or NaOH in Me_2SO give only traces of products of vicarious substitution of hydrogen. In analogy to the nitriles, esters of α-thio substituted acids were expected to be more efficient reactants, and **5**, **6**, and **7** were found to react readily with nitroarenes by vicarious substitution to give esters of α-(4-nitroaryl)alkanoic acids.

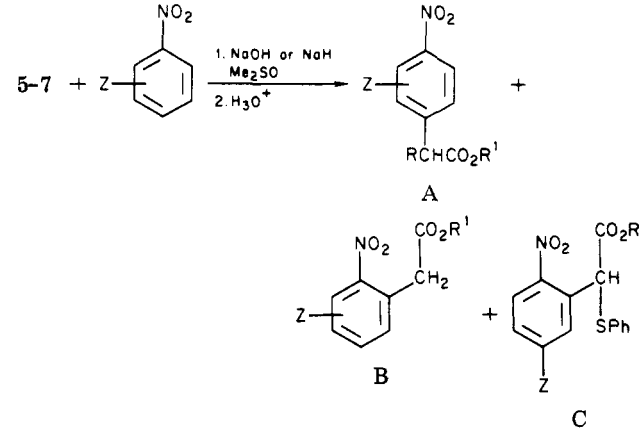


(4)

	R	X	R'
5b	H	PhS	Me
5c	H	Me_2NCS_2	Me
6b	H	PhS	*t*-Bu
6c	H	Me_2NCS_2	*t*-Bu
7	Me	PhS	*t*-Bu

Since methyl esters are more sensitive to alkaline hydrolysis than the corresponding nitriles, the reactions of these esters were carried out in the presence of NaH in Me_2SO, whereas reactions of the *tert*-butyl esters were run with sodium hydroxide in Me_2SO. Results are given in Table VI, and physical characteristics of the products are given in the Experimental Section. The yields of products

Table VI. Reactions of Nitroarenes with 5-7



Z	ester	product	yield,[a] %
H	**5b**	A	41
H	**5c**	A	27
4-Cl	**5c**	B	52[b]
H	**6b**	A	42
3-Cl	**6b**	A	66
C_4H_4[c]	**6b**	B	77
4-PhS	**6b**	B	14
		C	11
4-PhCO	**6b**	C	30
4-Cl	**6c**	B	49[b]
H	7	A	44
3-Cl	7	A	42

[a] Yields of isolated compounds. [b] A 50% molar excess of ester was used. [c] 1-Nitronaphthalene.

are usually lower than those from the corresponding nitriles.

As we have pointed out, the orientation in the vicarious nucleophilic substitution of hydrogen depends strongly on steric factors. Since carboalkoxy groups are bulkier than the cyano group, the reactions of secondary carbanions of esters **5–7** with nitrobenzene proceed exclusively at the para position. It is of interest to compare the orientation in reactions of esters and of nitriles containing different leaving groups with nitrobenzene. The values of the o/p ratios are $PhOCH_2CN$, 7.1, $ClCH_2CN$, 4.8, $PhSCH_2CN$, 0.91, and $PhSCH_2CO_2Me$, only para. Nevertheless, substitution at the ortho position by **5** and **6** does occur when the para position is occupied by a substituent such as Cl. Substitution at the ortho position also takes place in the reaction of **6b** with 1-nitronaphthalene. Like other carbanions containing leaving groups, carbanions of **5** and **6** replace hydrogen much faster than halogen located in an activated position.

In two reactions of **6b**, with 4-(phenylthio)nitrobenzene and with 4-(benzoyl)nitrobenzene, there were formed products of the direct nucleophilic substitution of hydride anion without elimination of the leaving group (Table VI). These products were apparently formed via oxidation of the intermediate σ complex by an external oxidant, probably Me_2SO or another molecule of the nitroarene. This interesting reaction is now under investigation. Reactions of this type have previously been observed with carbanions of ketones and nitriles.[9]

Experimental Section

Starting materials were commercially available or were prepared by known methods. ^1H NMR spectra were recorded on an JEOL-MH-100 spectrometer in $CDCl_3$ with Me_4Si as the internal

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standard. Chemical shifts are reported downfield from Me_4Si. Abbreviations of the multiplicity of the signals are s singlet, d doublet, dd doublet of doublets, t triplet, q quartet, m multiplet; m and p proton couplings are omitted. IR spectra were recorded on a UR-100 Zeiss-Jena spectrometer in $CHCl_3$. GC analyses were accomplished on a Gedeon GCHF 18.3 instrument using columns packed with 5% silicon OV-17 or OV-101 on Chromosorb. Column chromatography was accomplished on silica gel using hexane–chloroform or hexane–benzene mixtures as eluents. Reactions were carried out by one of the following procedures. Exceptions from these general methods are noted in the tables. All new compounds gave satisfactory microanalyses.

Procedure A (Sodium Hydroxide, Liquid Ammonia). A solution of chloroacetonitrile (0.01 mol) and nitroarene (0.01 mol) in 10 mL of ether was added dropwise to a vigorously stirred suuspension of powdered NaOH (4 g, 0.1 mol) in ca. 20 mL of liquid ammonia. The reaction was carried out −30 to −50 °C for 1 h. Ammonia was evaporated, the residue was dissolved in water and acidified with hydrochloric acid, and the products were extracted with methylene chloride. The extracts were washed with water and dried and the solvent was evaporated. The residue was chromatographed.

Procedure B (Sodium Hydroxide, Me_2SO). A solution of nitrile **1–4** or ester **6–7** (0.01 mol) and nitroarene (0.01 mol) in 10 mL of Me_2SO was added dropwise to a vigorously stirred suspension of powdered NaOH (4 g, 0.1 mol) in 10 mL of Me_2SO. The addition results in deep coloration (red, blue or violet) of the mixture and exothermic reaction. The temperature was kept below 30 °C with external cooling when necessary. The reaction was carried out at the room temperature for 1 h, the mixture was poured into ice–hydrochloric acid, and the products were extracted with methylene chloride or chloroform. The extracts were washed with water and dried, and the solvent was evaporated. The residue was chromatographed.

Procedure C (Sodium Hydride, Me_2SO). The reactions of esters **5** with nitroarenes were carried out according to Procedure B, using sodium hydride (0.022 mol) instead of sodium hydroxide. Reaction mixtures were poured onto ice and then acidified with acetic acid.

Product (procedure, Table): physical properties.

(2-Nitrophenyl)acetonitrile (A, B, I, III): mp 81–83 °C (lit.[10] mp 81.5–82.5 °C).

(4-Nitrophenyl)acetonitrile (A, B, I, III): mp 114–116 °C (lit.[10] mp 116 °C).

(3-Chloro-2-nitrophenyl)acetonitrile (A, I): mp 61–63 °C (ethanol); NMR δ 3.77 (s, 2 H), 7.53 (s, 3 H); IR 1365, 1540 (NO_2), 2260 (CN).

(3-Chloro-4-nitrophenyl)acetonitrile (A, I): mp 49–50 °C (benzene–hexane); NMR δ 3.90 (s, 2 H), 7.37 (d, 1 H), 7.53 (s, 1 H), 7.88 (d, 1 H); IR 1355, 1540 (NO_2), 2270 (CN).

(2-Chloro-6-nitrophenyl)acetonitrile (A, B, I, eq 3): mp 68–70 °C (ethanol); NMR δ 4.25 (s, 2 H), 7.59 (t, 1 H), 7.85 (d, 1 H), 8.08 (d, 1 H); IR 1355, 1540 (NO_2), 2270 (CN).

(4-Chloro-2-nitrophenyl)acetonitrile (B, eq 3): mp 86–88 °C (methanol); NMR δ 4.26 (s, 2 H), 7.78 (s, 2 H), 8.28 (s, 1 H); IR 1350, 1540 (NO_2), 2265 (CN).

(2-Chloro-4-nitrophenyl)acetonitrile (A, B, I, eq 3): mp 76–77.5 °C (ethanol); NMR δ 4.03 (s, 2 H), 7.73 (d, 1 H), 8.25 (d, 1 H), 8.25 (d, 1 H), 8.35 (s, 1 H); IR 1355, 1530 (NO_2), 2270 (CN).

(5-Chloro-2-nitrophenyl)acetonitrile (A, B, I, IV): mp 94–95.5 °C (ethanol); NMR δ 4.18 (s, 2 H), 7.52 (d, 1 H), 7.71 (s, 1 H), 8.14 (d, 1 H); IR 1350, 1530 (NO_2), 2260 (CN).

(5-Methoxy-2-nitrophenyl)acetonitrile (B, IV): mp 82–84 °C; (lit.[11] mp 84 °C); NMR δ 3.91 (s, 3 H), 4.21 (s, 2 H), 6.96 (d, 1 H), 7.14 (s, 1 H), 8.21 (d, 1 H); IR 1345, 1525 (NO_2) 2270 (CN).

(5-Ethoxy-2-nitrophenyl)acetonitrile (B, IV): mp 78–81 °C (ethanol); NMR δ 1.46 (t, 3 H), 4.16 (q, 2 H), 4.21 (s, 2 H), 6.94 (d, 1 H), 7.16 (s, 1 H), 8.22 (d, 1 H); IR 1345, 1520 (NO_2) 2265 (CN).

(5-(Methylthio)-2-nitrophenyl)acetonitrile (B, IV): mp 90–93 °C (ethanol); NMR δ 2.55 (s,S H), 4.19 (s, 2 H), 7.27 (d, 1 H), 7.44 (s, 1 H), 8.11 (d, 1 H); IR 1340, 1520 (NO_2) 2270 (CN).

[2-Nitro-5-(phenylthio)phenyl]acetonitrile (B, IV): mp 104–105 °C (ethanol); NMR δ 4.11 (s, 2 H), 7.09 (d, 1 H), 7.33 (s, 1 H), 7.51 (s, 5 H), 8.03 (d, 1 H); IR 1340, 1520 (NO_2), 2270 (CN).

(5-*tert*-Butyl-2-nitrophenyl)acetonitrile (B, IV): mp 58–60.5 °C (ethanol); NMR δ 1.35 (s, 9 H), 4.20 (s, 2 H), (7.53 (d, 1 H); IR 1350, 1530 (NO_2) 2265 (CN).

(4-Nitro-3-biphenylyl)acetonitrile (B, IV): mp 123–124 °C (ethanol); NMR δ 4.24 (s, 2 H), 7.42–7.77 (m, 6 H), 7.90 (s, 1 H), 8.25 (d, 1 H); IR 1350, 1530 (NO_2) 2260 (CN).

(1-Nitro-2-naphthyl)acetonitrile (A, B, I, III): mp 121.5–123 °C (ethanol); NMR δ 3.92 (s, 2 H), 7.5–8.1 (m, 6 H); IR 1350, 1530 (NO_2), 2260 (CN). Hydrolysis of that compound with an acetic (20 mL) hydrochloric acid (8 mL) mixture gave 1-nitro-2-naphthylacetic acid, mp 208–210 °C (lit.[12] mp 206–207 °C).

(4-Nitro-1-naphthyl)acetonitrile (A, B, I, III): mp 140.5–141 °C (ethanol); NMR δ 4.18 (s, 2 H), 7.62–8.14 (m, 5 H), 8.46–8.56 (m, 1 H); IR 1350, 1525 (NO_2), 2265 (CN). This compound was identical with (4-nitro-1-naphthyl)acetonitrile (TLC, NMR, mp 142–144 °C) obtained from (4-nitro-1-naphthyl)acetic acid[13] by action of (1) PCl_3, (2) NH_3, and (3) $SOCl_2$ in pyridine.

(4-Nitrophenyl)(phenylthio)acetonitrile (B, IVb): mp 57–60 °C (ethanol); NMR δ 4.89 (s, 1 H), 7.30–7.44 (m, 7 H), 8.12 (d, 2 H); IR 1355, 1535 (NO_2), 2250 (CN).

2-(4-Nitrophenyl)propionitrile (B, II, V): mp 72–74 °C; (lit.[14] mp 73–75 °C); NMR δ 1.74 (d, 3 H), 4.15 (q, 1 H), 7.68 (d, 2 H), 8.35 (d, 2 H).

2-(5-Chloro-2-nitrophenyl)propionitrile (B, II): mp 93–95.5 °C (ethanol); NMR δ 1.78 (d, 3 H), 4.85 (q, 1 H), 7.58 (d, 1 H), 7.86 (s, 1 H), 8.13 (d, 1 H); IR 1350, 1530 (NO_2), 2260 (CN).

2-(3-Chloro-4-nitrophenyl)propionitrile (B, II, V): oil; NMR 1.75 (d, 3 H), 4.08 (q, 1 H), 7.48 (d, 1 H), 7.60 (s, 1 H), 7.95 (d, 1 H); IR 1355, 1540 (NO_2), 2250 (CN).

2-(3-Fluoro-4-nitrophenyl)propionitrile (B, II): mp 55.5–56.5 °C (ethanol); NMR δ 1.76 (d, 3 H), 4.09 (q, 1 H), 7.3–7.5 (m, 2 H), 8.20 (t, 1 H); IR 1355, 1540 (NO_2), 2260 (CN).

2-[4-Nitro-3-(phenylthio)phenyl]propionitrile (B, V): mp 80–82 °C (ethanol); NMR δ 1.45 (d, 3 H), 3.70 (q, 1 H), 6.78 (s, 1 H), 7.15 (d, 1 H), 7.55 (s, 5 H), 8.19 (d, 1 H); IR 1350, 1530 (NO_2), 2260 (CN).

2-(4-Nitro-1-naphthyl)propionitrile (B, V): mp 62.5–64 °C (ethanol): NMR δ 1.81 (d, 3 H), 4.83 (q, 1 H), 7.60–8.18 (m, 5 H), 8.33–8.40 (m, 1 H); IR 1350, 1525 (NO_2), 2255 (CN).

2-(4-Nitrophenyl)isovaleronitrile (B, II, V): 71–74 °C (ethanol); NMR δ 1.05 (dd, 6 H), 2.17 (m, 1 H), 3.79 (d, 1 H), 7.48 (d, 2 H), 8.23 (d, 4 H); IR 1350, 1530 (NO_2), 2250 (CN).

2-(5-Chloro-2-nitrophenyl)isovaleronitrile (B, II): mp 77–79 °C (ethanol); NMR δ 1.15 (dd, 6 H), 2.22 (m, 1 H), 4.87 (d, 1 H), 7.61 (d, 1 H) 7.83 (s, 1 H), 8.15 (d, 1 H); IR 1350, 1530 (NO_2), 2260 (CN).

2-(3-Chloro-4-nitrophenyl)isovaleronitrile (B, II): oil; bp 144–146 °C (0.2 mmHg); NMR δ 1.06 (dd, 6 H), 2.16 (m, 1 H), 3.78 (d, 1 H), 7.39 (d, 1 H), 7.52 (s, 1 H), 7.90 (d, 1 H); IR 1350, 1535 (NO_2) 2250 (CN).

2-(2-Chloro-4-nitrophenyl)isovaleronitrile (B, V): mp 49–50 °C (ethanol); NMR δ 1.13 (dd, 6 H), 2.26 (m, 1 H), 4.27 (d, 1 H), 7.74 (d, 1 H), 8.13–8.28 (m, 2 H); IR 1355, 1530 (NO_2), 2260 (CN).

2-(3-Methoxy-4-nitrophenyl)isovaleronitrile (B, V): mp 63.5-64.5 °C (ethanol); NMR δ 1.05 (dd, 6 H), 2.16 (m, 1 H), 3.70 (d, 1 H), 3.95 (s, 3 H), 6.88–6.98 (m, 2 H), 7.82 (d, 1 H); IR 1360, 1530 (NO_2), 2260 (CN).

2-(4-Nitro-1-naphthyl)isovaleronitrile (B, V): mp 134–137 °C (ethanol); NMR δ 1.11 (dd, 6 H), 2.30 (m, 1 H), 4.52 (d, 1 H), 7.66–8.18 (m, 5 H), 8.44–8.57 (m, 1 H); IR 1350, 1525 (NO_2), 2260 (CN).

α-(4-Nitrophenyl)phenylacetonitrile (B, V): mp 69–70 °C (lit.[15] mp 70–72 °C); NMR δ 5.24 (s, 1 H), 7.35 (s, 5 H), 7.52 (d, 2 H), 8.18 (d, 2 H); IR 1350, 1530 (NO_2), 2260 (CN).

α-(3-Chloro-4-nitrophenyl)phenylacetonitrile (B, V): mp 54–57 °C (methanol); NMR δ 5.16 (s, 1 H), 7.28–7.44 (m, 6 H), 7.51 (s, 1 H), 7.86 (d, 1 H); IR 1350, 1530 (NO_2) 2250 (CN).

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α-(4-Nitro-1-naphthyl)phenylacetonitrile: mp 117–121 °C (methanol); NMR δ 5.87 (s, 1 H), 7.34 (s, 5 H), 7.57–8.18 (m, 5 H), 8.69–8.44 (m, 1 H); IR 1350, 1530 (NO_2), 2260 (CN).

Methyl (4-nitrophenyl)acetate (C, VI): mp 53–55 °C (lit.[16] mp 52.4–53.3 °C); NMR δ 3.64 (s, 5 H), 7.41 (d, 2 H), 8.12 (d, 2 H); IR 1355, 1530 (NO_2) 1745 (CO).

Methyl (5-chloro-2-nitrophenyl)acetate (C, VI): oil (lit.[17]); NMR δ 3.69 (s, 3 H), 3.96 (s, 2 H), 7.31–7.48 (m, 2 H), 8.05 (d, 1 H); IR 1350, 1530 (NO_2), 1740 (CO).

***tert*-Butyl (4-nitrophenyl)acetate** (B, VI): mp 34–36 °C (lit.[18] mp 37–38 °C); NMR δ 1.43 (s, 9 H), 3.61 (s, 2 H), 7.42 (d, 2 H), 8.16 (d, 2 H); IR 1350, 1525 (NO_2), 1730 (CO).

***tert*-Butyl (2-chloro-4-nitrophenyl)acetate** (B, VI): mp 49–52 °C (ethanol); NMR δ 1.43 (s, 9 H), 3.75 (s, 2 H), 7.46 (d, 1 H), 8.06 (d, 1 H), 8.22 (s, 1 H); IR 1355, 1525 (NO_2), 1730 (CO).

***tert*-Butyl (1-nitro-2-naphthyl)acetate** (B, VI): mp 97–98 °C (ethanol); NMR δ 1.43 (s, 9 H), 3.71 (s, 2 H), 7.1–7.9 (m, 6 H); IR 1525 (NO_2), 1730 (CO). Hydrolysis in acetic acid–hydrochloric acid mixture gave (1-nitro-2-napthyl)acetic acid, mp 209–212 °C (lit.[13] mp 206–207 °C).

***tert*-Butyl [2-nitro-5-(phenylthio)phenyl]acetate** (B, VI): mp 62–63 °C; NMR δ 1.50 (s, 9 H), 3.89 (s, 2 H), 7.03–7.13 (m, 2 H), 7.53 (s, 5 H), 8.00 (d, 1 H); IR 1345, 1520 (NO_2,) 1730 (CO).

***tert*-Butyl 2-[2-nitro-5-(phenylthio)phenyl](phenylthio)acetate** (B, VI): oil; NMR δ 1.27 (s, 9 H), 5.39 (s, 1 H), 6.95–7.45 (m, 12 H), 7.75 (d, 1 H); IR 1345, 1520 (NO_2), 1730 (CO).

***tert*-Butyl 2-(5-benzoyl-2-nitrophenyl)(phenylthio)acetate** (B, VI): mp 80–81.5 °C; NMR δ 1.36 (s, 9 H), 5.44 (s, 1 H), 7.15–8.15 (m, 13 H); IR 1355, 1530 (NO_2), 1670 (CO).

***tert*-Butyl (5-chloro-2-nitrophenyl)acetate** (B, VI): mp 61–63 °C; NMR δ 1.48 (s, 9 H), 3.99 (s, 2 H), 7.30–7.45 (m, 2 H), 8.04 (d, 1 H); IR 1350, 1530 (NO_2), 1735 (CO).

***tert*-Butyl 2-(4-nitrophenyl)propionate** (B, VI): oil; NMR δ 1.36–1.42 (m, 12 H), 3.63 (q, 1 H), 7.41 (d, 2 H), 8.12 (d, 2 H); IR 1355, 1525 (NO_2) 1730 (CO).

***tert*-Butyl 2-(2-chloro-4-nitrophenyl)propionate** (B, VI): oil; NMR δ 1.45–1.50 (m, 12 H), 4.20 (q, 1 H), 7.54 (d, 1 H), 8.15 (d, 1 H), 8.30 (s, 1 H); IR 1360, 1530 (NO_2), 1730 (CO).

(5-Chloro-2-nitrophenyl)acetonitrile.[19] To a solution of *p*-chloronitrobenzene (8 g, 0.05 mol) in dry ether (50 mL) was added liquid ammonia (ca. 120 mL) followed by powdered NaOH (10 g, 0.25 mol) and the whole mixture stirred for 10 min. To the stirred mixture was added a solution of chloroacetonitrile (4.2 g, 0.055 mol) in ether (10 mL) dropwise during 40 min. After the addition was completed the reaction was carried out for 1 h, and then NH_4Cl (10 g) was added portionwise and ammonia evaporated on a water bath. During the evaporation CCl_4 (ca. 120 mL) was added portionwise so the volume was kept approximately constant. Finally the bath temperature was raised and ether distilled off until the CCl_4 began to reflux. The warm mixture was filtered and the solid was refluxed with two portions of CCl_4 (120 mL) and filtered. The combined filtrates were evaporated and the residue boiled with hexane (100 mL) and filtered to give pure product (mp 89–90 °C, 7.8 g). An additional 0.6 g of the product was isolated from the hexane solution. The total yield was 8.4 g, 75%.

2-(1-Nitro-2-naphthyl)propionitrile. 1-Nitro-2-naphthylacetonitrile (1 g, 4.7 mmol), methyl iodide (0.7 g), K_2CO_3 (2 g), and acetone (20 mL) were stirred and refluxed for 4 h. Inorganic salts were filtered off, the solvent was evaporated, and the residue was chromatographed to give 0.85 g, (80%) of the product: mp 92.5–95 °C (ethanol); NMR δ 1.78 (d, 3 H), 4.20 (q, 1 H), 7.63–8.18 (m, 6 H); IR 1365, 1535 (NO_2), 2265 (CN).

4-Nitro-1-naphthyl Phenyl Ketone. Hydrogen peroxide (30%, 20 mL) was added in several portions to a mixture of δ-(4-nitro-1-naphthyl)phenylacetonitrile (1 g), sodium hydroxide (3 g), methanol 20 mL), and water (20 mL). The solution was kept at room temperature for 10 h. Then the precipitate was filtered and recristallized from ethanol to give 0.5 g of the title compound: mp 83–84.5 °C; IR 1350, 1530 (NO_2), 1670 (CO) cm^{-1}.

4-(*N*-Actylamino)-1-naphthyl Phenyl Ketone. 4-Nitro-1-naphthyl phenyl ketone (0.5 g), acetic acid (50 mL), acetic anhydride (10 mL), and iron powder (3 g) were refluxed for 5 h. The solution was filtered and diluted with water; the product filtered and recrystallized from ethanol to give 0.3 g of the title compound, mp 158–161 °C (lit.[20] mp 159–161 °C).

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Registry No. **1a**, 107-14-2; **1b**, 5219-61-4; **1c**, 61540-35-0; **1d**, 35928-65-5; **1e**, 3598-14-9; **2a**, 1617-17-0; **2b**, 33695-43-1; **3a**, 70477-21-3; **3b**, 89278-07-9; **4e**, 32121-27-0; **4f**, 89278-08-0; **4g**, 72301-64-5; **4h**, 13031-13-5; **5b**, 17277-58-6; **5c**, 27888-12-6; **6b**, 63006-68-8; **6c**, 89278-15-9; **7**, 89278-16-0; $C_6H_5NO_2$, 98-95-3; 2-$ClC_6H_4NO_2$, 88-73-3; 3-$ClC_6H_4NO_2$, 121-73-3; 4-$ClC_6H_4NO_2$, 100-00-5; 2-$FC_6H_4NO_2$, 1493-27-2; 4-$FC_6H_4NO_2$, 350-46-9; 4-$MeOC_6H_4NO_2$, 100-17-4; 4-$EtOC_6H_4NO_2$, 100-29-8; 4-$MeSC_6H_4NO_2$, 701-57-5; 4-$PhSC_6H_4NO_2$, 952-97-6; 4-*t*-$BuC_6H_4NO_2$, 3282-56-2; 4-$PhC_6H_4NO_2$, 92-93-3; 2-$MeOC_6H_4NO_2$, 91-23-6; 4-$PhCOC_6H_4NO_2$, 1144-74-7; 2-$O_2NC_6H_4CH_2CN$, 610-66-2; 4-$O_2NC_6H_4CH_2CN$, 555-21-5; 3-Cl-2-$O_2NC_6H_3CH_2CN$, 77158-79-3; 3-Cl-4-$O_2NC_6H_3CH_2CN$, 80199-01-5; 2-Cl-6-$O_2NC_6H_3CH_2CN$, 89277-98-5; 2-Cl-4-$O_2NC_6H_3CH_2CN$, 89277-99-6; 4-Cl-2-$O_2NC_6H_3CH_2CN$, 87081-90-1; 5-Cl-2-$O_2NC_6H_3CH_2CN$, 72301-65-6; 4-$O_2NC_6H_4CH(CH_3)CN$, 50712-63-5; 3-Cl-4-$O_2NC_6H_3CH(CH_3)CN$, 86981-07-9; 3-F-4-$O_2NC_6H_3CH(CH_3)CN$, 85397-18-8; 5-Cl-2-$O_2NC_6H_3CH(CH_3)CN$, 89278-01-3; 4-$O_2NC_6H_4CH(CN)CHMe_2$, 81310-40-9; 3-Cl-4-$O_2NC_6H_3CH(CN)CHMe_2$, 89278-02-4; 5-Cl-2-$O_2NC_6H_3CH(CN)CHMe_2$, 89278-03-5; 5-PhS-2-$O_2NC_6H_3CH_2CN$, 72301-69-0; 5-MeO-2-$O_2NC_6H_3CH_2CN$, 89302-15-8; 5-EtO-2-$O_2NC_6H_3CH_2CN$, 89278-04-6; 5-MeS-2-$O_2NC_6H_3CH_2CN$, 72301-70-3; 5-*t*-Bu-2-$O_2NC_6H_3CH_2CN$, 89278-05-7; 5-Ph-2-$O_2NC_6H_3CH_2CN$, 72301-68-9; 4-$O_2NC_6H_4CH(CN)SPh$, 89278-06-8; 3-PhS-4-$O_2NC_6H_3CH(CH_3)CN$, 89278-14-8; 2-Cl-4-$O_2NC_6H_3CH(CN)CHMe_2$, 89278-10-4; 3-MeO-4-$O_2NC_6H_3CH(CN)CHMe_2$, 89278-11-5; 4-$O_2NC_6H_4CH(Ph)CN$, 7599-05-5; 3-Cl-4-$O_2NC_6H_3CH(Ph)CN$, 89278-13-7; 4-$O_2NC_6H_4CH_2CO_2Me$, 2945-08-6; 5-Cl-2-$O_2NC_6H_3CH_2CO_2Me$, 22908-29-8; 4-$O_2NC_6H_4CH_2CO_2Bu$-*t*, 29704-38-9; 2-Cl-4-$O_2NC_6H_3CH_2CO_2Bu$-*t*, 89278-17-1; 5-PhS-2-$O_2NC_6H_3CH_2CO_2Bu$-*t*, 89278-19-3; 5-PhS-2-$O_2NC_6H_3CH(SPh)CO_2Bu$-*t*, 89278-20-6; 5-PhCO-2-$O_2NC_6H_3CH(SPh)CO_2Bu$-*t*, 89278-21-7; 5-Cl-2-$O_2NC_6H_3CH_2CO_2Bu$-*t*, 81327-28-8; 4-$O_2NC_6H_4CH(CH_3)CO_2Bu$-*t*, 89278-22-8; 2-Cl-4-$O_2NC_6H_3CH(CH_3)CO_2Bu$-*t*, 89278-23-9; 1-nitronaphthalene, 86-57-7; 1-nitro-2-naphthylacetonitrile, 89278-00-2; 1-nitro-2-naphthylacetic acid, 89278-24-0; 4-nitro-1-naphthylacetonitrile, 72301-67-8; 4-nitro-1-naphthylacetic acid, 89278-25-1; 2-(4-nitro-1-naphthyl)propionitrile, 89278-09-1; 2-(4-nitro-1-naphthyl)isovaleronitrile, 89278-12-6; α-(4-nitro-1-naphthyl)phenylacetonitrile, 72301-66-7; *tert*-butyl (1-nitro-2-naphthyl)acetate, 89278-18-2; 2-(1-nitro-2-naphthyl)propionitrile, 89278-26-2; 4-nitro-1-naphthyl phenyl ketone, 89278-27-3; 4-(*N*-acetylamino)-1-naphthyl phenyl ketone, 89278-28-4.

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