Vicarious Nucleophilic Substitution of Hydrogen in Nitroarenes with Carbanions of α-Haloalkyl Phenyl Sulfones[1]

Mieczysław Makosza* and Jerzy Goliński

Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland

Janusz Baran

Institute of Fundamental Chemistry, Technical University, Szczecin, Poland

Received April 4, 1983

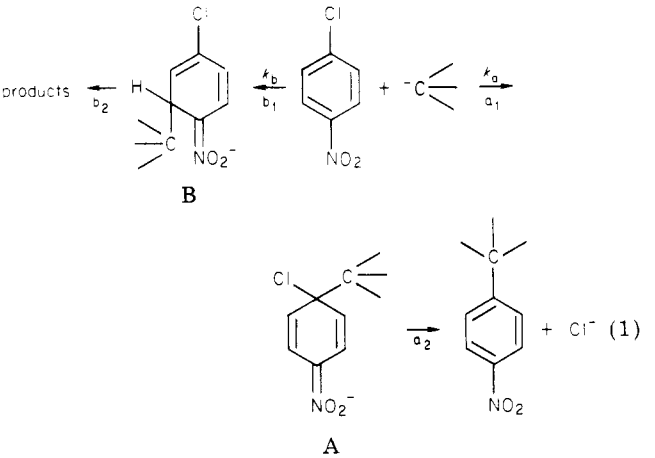
Carbanions of α-chloroalkyl phenyl sulfones and *N,N*-dialkyl-α-chloroalkanesulfonamides react with nitrobenzenes to effect direct nucleophilic replacement of hydrogen ortho and para to the nitro group, with vicarious loss of chloride anion, to give the corresponding nitrobenzylsulfonyl derivatives. The reaction occurs much more rapidly than the replacement of such good leaving groups as halogen, methoxy, and phenoxy. Most substituents in the nitrobenzene ring do not interfere with the reaction. The effect of substituents in the nitrobenzene and the carbanion on the orientation of the substitution is discussed.

Introduction

Nucleophilic substitution of halogen or other nucleofugal groups located para or ortho to the nitro group in nitroaromatic compounds proceeds by an addition–elimination mechanism.[2] A nucleophile adds to the carbon atom of the aromatic ring bearing a nucleofugal substituent with the formation of an intermediate cyclohexadiene nitronate anion known as a σ, or Meisenheimer, complex. The latter loses the nucleofugal substituent as an anion with simultaneous restoration of the aromatic system, giving the product. Nucleophilic replacement of halogen in halonitroarenes by carbanions follows the same mechanistic scheme, but the course of the reaction is often complicated by electron-transfer[3] or intra- or intermolecular redox processes.[4,5]

Addition of carbanions to halonitroarenes occurs because of the powerful electron-withdrawing nitro group. It is therefore reasonable to expect that this addition should take place not only at halogen-bearing carbon atoms para and ortho to the nitro group but also at hydrogen-bearing carbon atoms in these positions. Hence, in the case of *p*-chloronitrobenzene, for example, two possible complexes A and B can, in principle, be formed (eq 1).

Complex A loses chloride anion rapidly to form the typical product of nucleophilic substitution. The fate of complex B is much less predictable. It cannot lose the hydride anion, which is a very poor leaving group, so in contrast to A, the formation of B should be in principle a reversible process. Further transformation of B could involve an intramolecular redox reaction at the expense of the nitro group.[4a,4b,5] In such a reaction the competition between nucleophilic replacement of a leaving group and oxidative replacement of hydrogen is usually governed by the nature of the base–solvent system.



Because the formation of complex A is usually an irreversible process, the formation of products derived from complex B requires that the addition according to pathway b be much faster than that via a ($k_b > k_a$) (eq 1). A direct comparison of the rates of formation of A and B complexes from mononitroarenes has not been made since these complexes are short-lived species. Such comparison has been made for polynitroarenes such as trinitroanisole, where a general rule was found that nucleophiles add rapidly to positions bearing hydrogen with the formation of B complexes, which rearrange less rapidly to the more stable A complexes.[6] If this observation applies to mononitroarenes, then the relation $k_b > k_a$ is a general one. Nucleophilic substitution in aromatic nitro compounds can therefore be pictured as proceeding by an initial rapid, reversible addition of a nucleophile to a hydrogen-bearing carbon atom ortho or para to the nitro group to form a B complex. In rather infrequent cases where there is a fast step by which complex B can be transformed into products, the reaction follows path b. In general, however, complex B reverts to the starting components and then, via slower but irreversible formation of complex A, a nucleofugal substituent is replaced. If there was a fast general step by which complexes B could be transformed into stable products, path b would be the main reaction course. Although oxidation of B by external oxidants seems an attractive solution to this problem, it is usually infeasible for mononitroarenes because the concentration of complex

(1) Part 109 of the Series Reactions of Organic Anions; part 108, ref 13.

(2) Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273. Miller J. "Aromatic Nucleophilic Substitution"; Elsevier: New York, 1968. De Boer, Th. J.; Dirks, J. P. "Chemistry of the Nitro and Nitroso Group"; Feuer, H., Ed.; Interscience: New York, 1969; Chapter 8. Bernasconi, C. F. *Chimia* **1980**, *34*, 1.

(3) Russel, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807. Guthrie, R. D.; Hrovat, D. A.; Prahl, F. G.; Swan, I. *J. Org. Chem.* **1981**, *46*, 498.

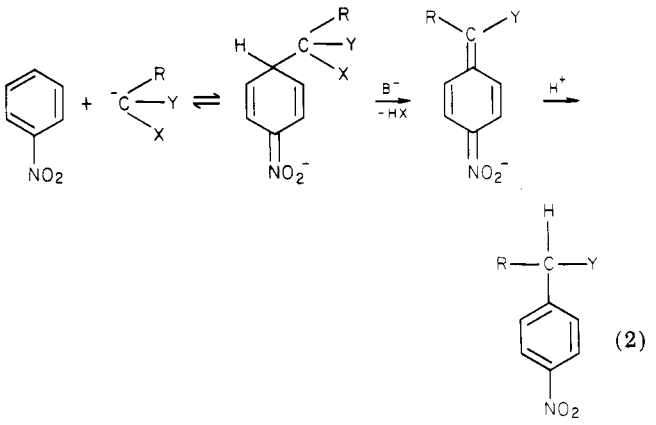
(4) (a) Davis, R. B.; Pizzini, L. C. *J. Org. Chem.* **1960**, *25*, 1884. Davis, R. B. Pizzini, L. C.; Bara, E. J. *Ibid.* **1961**, *26*, 4270. (b) Mąkosza, M.; Jagusztyn-Grochowska, M.; Ludwikow, M.; Jawdosiuk, M. *Tetrahedron* **1974**, *30*, 3723.

(5) Mąkosza, M.; Zielińska, A. *Rocz. Chem.* **1972**, *46*, 955. Marey, T. Fournari, D.; Tirouflet, J. *C. R. Hebd. Seances Acad. Sci.* **1965**, *260*, 4340.

(6) Servis, K. L. *J. Am. Chem. Soc.* **1967**, *89*, 1508. Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667. Terrier, A. *Chem. Rev.* **1982**, *82*, 77. Artamkina, O. A.; Egorov, M. P.; Beletskaya, I. P. *Ibid.* **1982**, *82*, 427.

0022-3263/84/1949-1488$01.50/0

B in the system is very low, and because of the sensitivity of carbanions toward oxidation. Although there are a few reports of oxidations of B complexes with oxidizing substituents in the nitroarene molecule[7] or with external oxidants,[8] these examples are not generally applicable. We have formulated a concept of a reaction by which B complexes can be converted into products,[9-12] based on the use of carbanions containing leaving groups X at the carbanion center. Departure of the leaving group from such a B complex should form the product of nucleophilic replacement of hydrogen in the nitroarene (eq 2). Such a



(2)

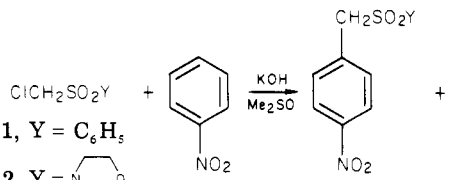
reaction requires a way for efficient removal of the hydride anion from complex B, and we have suggested that this could occur via a hydride shift.[9] However, experimental examination of the mechanism has revealed that the reaction occurs via base-induced β-elimination of HX from the B complex.[13]

There are a few earlier observations that can be considered as examples of this type of reaction. Traynellis[14] and Metzger[15] have described the methylation of nitroarenes with dimethylsulfoxonium methylide, which apparently occurs via a σ complex of type B and elimination of dimethyl sulfoxide. Methylation of nitrobenzene and some aromatic heterocycles with dimsylsodium[16] proceeds similarly with departure of methanesulfenate anion. Dichloromethylation of *p*-halonitrobenzenes with trichloromethyllithium[17] apparently proceeds via the addition of the CCl_3^- anion and elimination of HCl from the σ complex rather than by a dichlorocarbene reaction as suggested by the authors. The possibility of the nucleophilic replacement of hydrogen in nitrophenazines by a similar type of reaction has been considered.[18]

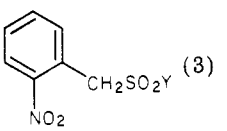
Our proposed reaction scheme requires a carbanion that does not react readily with its precursor—the CH acid RCHXY. Although some CH acids in which X = halogen are usually active alkylating agents, α-haloalkyl aryl sulfones are not.[19] We here report on the replacement of hydrogen in mononitroarenes by carbanions derived from some α-haloalkyl aryl sulfones and sulfonamides.

Results and Discussion

Mixing of chloromethyl phenyl sulfone (1) with nitrobenzene and a 3-fold excess of powdered potassium hydroxide in Me_2SO resulted in a strong exothermic reaction accompanied by deep blue-violet coloration of the mixture. Workup gave *o*- and *p*-nitrobenzyl phenyl sulfones in a total yield of 75%. A similar reaction occurred between nitrobenzene and chloromethyl 4-morpholinyl sulfone (2), a compound that also meets our formulated requirements (eq 3).



1, Y = C_6H_5
2, Y = morpholino
3
4
5

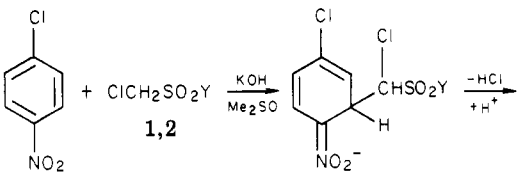


(3)

6
7

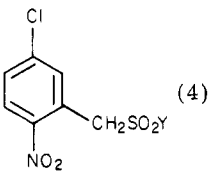
The reaction shown in eq 2 and 3 involves replacement of hydrogen in the ortho or para position of nitrobenzene by a carbanion moiety, with halogen from the carbanion center being eliminated from the intermediate σ complex. The leaving halogen anion acts as a vicarious leaving group, and we term the process "vicarious nucleophilic substitution of hydrogen".[9]

According to our concept the reaction of carbanions of 1 and 2 with *p*-chloronitrobenzene (**8a**) should result in the replacement of hydrogen rather than halogen (eq 4).



1,2

8a



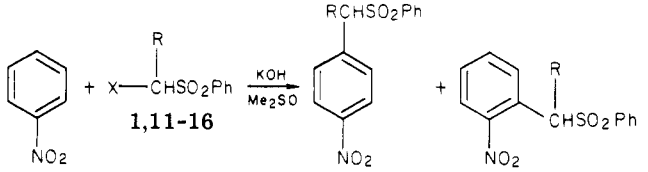
(4)

9a, Y = C_6H_5
10a, Y = morpholino

We find that both 1 and 2 react smoothly with **8a** in the presence of KOH in Me_2SO to give the corresponding 3-chloro-5-nitrobenzyl phenyl sulfone **9a** and 4-morpholinyl sulfone **10a** without any products of the substitution of halogen. In separate experiments it was shown that the products that would be formed by replacement of halogen are stable under the reaction conditions. These results confirm the relation of the rate constants $k_b > k_a$ (eq 1)

(7) Pietra, S.; Casiragni, G. *Gazz. Chim. Ital.* **1966**, *96*, 1630; *Ibid.* **1967**, *97*, 1826. Richter, H. J.; Rustad, N. E. *J. Org. Chem.* **1964**, *29*, 3381.
(8) Kienzle, F. *Helv. Chim. Acta* **1978**, *61*, 449. Iwasaki, G.; Hamana, M.; Saeki, S. *Heterocycles* **1982**, *19*, 162. Hamana, M.; Iwasaki, G.; Saeki, S. *Heterocycles* **1982**, *17*, 177. Chupakhin, O. N.; Postovskii, I. Ya. *Usp. Khim.* **1976**, *65*, 908.
(9) Goliński, J.; Mąkosza, M. *Tetrahedron Lett.* **1978**, 3495.
(10) Mąkosza, M.; Goliński, J. *Angew. Chem.* **1982**, *94*, 468.
(11) Mąkosza, M.; Goliński, J.; Pankowski, J. *Synthesis* **1983**, 40.
(12) Mąkosza, M.; Winiarski, J. *J. Org. Chem.* **1980**, *45*, 1534.
(13) Mąkosza, M.; Glinka, T. *J. Org. Chem.* **1983**, *48*, 3860.
(14) Traynellis, V. J.; McSweeney, J. V. *J. Org. Chem.* **1966**, *31*, 243.
(15) Metzger, H.; König, H.; Seelert, K. *Tetrahedron Lett.* **1964**, 867.
(16) Russell, A. G.; Weiner, S. A. *J. Org. Chem.* **1966**, *31*, 243.
(17) McBee, E. T.; Wesseler, E. P.; Hodgins, T. *J. Org. Chem.* **1971**, *36*, 2907.
(18) Pietra, S.; Casiragni, G.; Selva, A. *Ann. Chim. (Roma)* **1968**, *58*, 1380.
(19) Bordwell, F. G.; Brannen, W. T. *J. Am. Chem. Soc.* **1964**, *86*, 4645.

Table I. Orientation of Hydrogen Substitution in Nitrobenzene



3 4, 17-19 6

sulfone	X	R	product	total yield,[a] %	ratio of isomers[b]	
11	F	H	4,6	63	26	74
1	Cl	H	4,6	75	47	53
12	Br	H	4,6	40	65	35
13	I	H	4,6	20	85	15
14	Cl	Et	17	68	100	
15	Cl	Ph	18	93	100	
16	Cl	Cl	19	35	100	

[a] Yields of isolated products. [b] Determined by GLC and by ^{1}H NMR signals of the methine protons.

and show that the vicarious substitution of hydrogen via nucleophilic attack of halomethylsulfonyl carbanions on nitroarenes proceeds much faster than the conventional substitution of chloride anion.

The second important feature of this reaction is that the products are stronger CH acids than the starting chloromethylsulfonyl compounds, and exist in the reaction mixture as highly colored nitrobenzylic carbanions. For this reason it is necessary to use at least a 2-fold excess of base in the reaction. This excess of base is necessary to achieve β-elimination of HCl from the σ complex.[13] Preliminary studies of reaction conditions have shown that the cation–carbanion interaction should be essentially ionic and that the degree of aggregation and cation–carbanion coordination should be low.[20] Thus the most useful base–solvent systems are KOH, NaOH, or *t*-BuOK in Me_2SO or liquid ammonia.

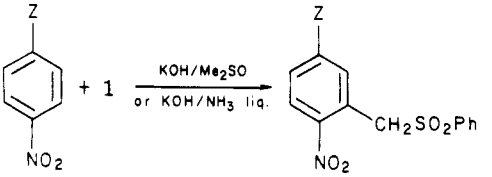
We investigated the orientation of substitution in nitrobenzene in reactions with α-halo sulfones $PhSO_2CHRX$, where R = H or alkyl and X = F, Cl, Br, and I, with the results shown in Table I. The results indicate that the ratio of ortho to para substitution is governed largely by steric factors. Methylenic carbanions (R = H) replace hydrogen in both ortho and para positions, the ratio of para:ortho substitution increasing with the size of the leaving halogen anion. Methinic carbanions (R ≠ H) replace hydrogen exclusively in the para position.

Next we studied the reaction of 1 with a variety of monosubstituted nitrobenzenes containing substituents located ortho, meta, or para to the nitro group.

The reaction of 1 with para-substituted nitrobenzenes can occur only in the ortho position so there are no problems with the formation and separation of isomeric products. The results (Table II) indicate that most electron-withdrawing and electron-donating substituents do not interfere with the course of the substitution. In a few cases the reaction proceeds in low yield or not at all. The electron-donating dimethylamino group decreases the electrophilic properties of the ring, so that nucleophilic addition of the carbanion is disfavored and the yield of product is low. However, other electron-donating groups such as MeO, PhO, and MeS do not affect the reaction and yields of the products are high. These substituents are relatively easily replaced by nucleophiles in an addition–elimination reaction. Nevertheless, in the reaction of **8c,d,i** with **1**, similar to that of **8a**, vicarious substitution of ortho hydrogen occurs, and replacement of RO or RS groups is not observed.

(20) Pankowski, J. Ph. D. Thesis, Technical University, Warsaw, 1983.

Table II. Reaction of *p*-Substituted Nitrobenzenes 8a-r with 1



8a-r 9a-r

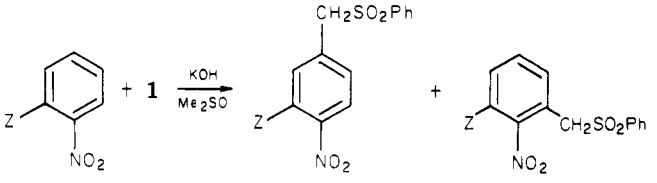
8	Z	product	yield,[a] %	mp, °C, solvent	procedure
a	Cl	9a	69	169-171, C_6H_6	C
b	NMe_2	9b	13	190-192, EtOH	C
c	OMe	9c	48	167-168.5, AcOH	C
d	OPh	9d	73	144-145, EtOH	C
e	Et	9e	22	86-89, EtOH	A
f	*t*-Bu	9f	71	144-146.5, EtOH	C
g		9g	76	140-142, C_6H_6	C
h	Ph	9h	57	157-158, C_6H_6	C
i	SMe	9i	72	155-157, C_6H_6	C
j	Br	9j	61	145-147, C_6H_6	C
k	I	9k	74	170-171.5, EtOH	C
l	F	9l	18[b]	135-137, EtOH	B
m	NO_2	9m	13[b]	212-214, EtOH	D
n	CN	9n	52	168-170, EtOH	D
o	CF_3	9o	85	142-143, EtOH	C
p	SO_2Me	9p	50	182-184, AcOH	C
r	COOH	9r	60	262-263, AcOH	C

[a] Yields of isolated products. [b] α-Chloro-4-nitrobenzyl phenyl sulfone **19** was also formed by nucleophilic substitution of F or NO_2; yields 27% and 6%, respectively.

p-Nitrotoluene reacts poorly with 1 because of the high acidity of the methyl group. The less acidic *p*-ethylnitrobenzene reacts more readily, although the yield is only moderate. On the other hand, *p*-(*tert*-butyl)nitrobenzene (**8f**), *p*-nitrobiphenyl (**8h**), and *p*-nitrobenzaldehyde ethylene acetal (**8g**) react satisfactorily.

In *p*-chloro-, *p*-bromo-, and *p*-iodonitrobenzenes the ortho hydrogen is replaced by the carbanion of 1. On the other hand, in *p*-fluoronitrobenzene substitution of both fluorine and hydrogen is observed. Both reactions are also observed with *p*-dinitrobenzene. It is known that F and NO_2 are very active leaving groups in aromatic nucleophilic substitution by addition–elimination.[2] The electron-withdrawing substituents CN, CF_3, and SO_2Me do not interfere with the course of the reaction. *p*-Nitrobenzoic acid, which reacts as the carboxylate anion, gives the expected product in good yield, although the reaction involves addition of a carbanion to an anion. On the other

Table III. Reaction of *o*-Substituted Nitrobenzenes 20a-g with 1

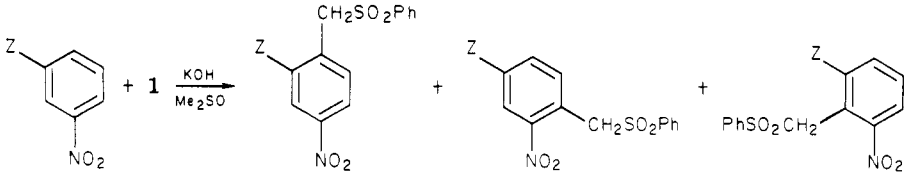


20a-g 21a-g 22a-g

20	Z	total yield,[a] (21 + 22)	ratio of isomers, %[b] (mp, °C, solvent) 21	22	procedure
a	Cl	85	65 (198-200, AcOH)	35 (144.5-147.5, EtOH)	C
b	NMe_2	61	84 (151-153, EtOH)	14 (144-145, EtOH)	A
c	OMe	71	80 (163-165, AcOH)	20 (133-135, EtOH)	A
d	OPh	79	80 (118.5-121, AcOH)	20 (110-112, EtOH)	C
e	Me	22[c]	81 (165-168, EtOH)	19	A
f	CF_3	67	50 (146.5-149, EtOH)	50 (165-166, EtOH)	A
g	NO_2	11[c]	(159-162, EtOH)		
h	*t*-Bu	no reaction			

[a] Yields of isolated mixtures of **21** and **22**. [b] Determined by ^1H NMR signals of the methylene protons. [c] Yields of isolated isomers **21e** and **21g**; **22e** was not isolated in a pure state.

Table IV. Reactions of *m*-Substituted Nitrobenzenes 23a-n with 1



23a-n 24a-l,n 25a-n 26a-e

23	Z	total yield,[a] % (24 + 25 + 26)	ratio of isomers, %[b] (mp, °C, solvent) 24	25	26	procedure
a	Me	64	80 (159-161, AcOH)	17 (113-114, EtOH)	3 (139-140, EtOH)	B
b	Cl	91	70 (146.5-148, AcOH)	25 (152-154, EtOH)	5 (144-146, EtOH)	B
c	Br	90	58 (155-156, EtOH)	37 (143-144, EtOH)	5 (135-136, EtOH)	B
d	OMe	53	66 (154-157, EtOH)	11 (97-100, EtOH)	22 (148-149, EtOH)	A
e	F	68	52 (177.5-179, MeOH)	10[c]	38 (156-157, MeOH)	B
f	NMe_2	51	80 (102-104, EtOH)	20 (144-145, EtOH)		B
g	OPh	74	85 (119-121, AcOH)	15 (113.5-115, EtOH)		B
h	I	64	69 (177-179.5, EtOH)	31 (126-128, EtOH)		B
i		74	50 (122-130, benzene)	50 (136-139, C_6H_6)		A
j	CN	72	35 (195-198, AcOEt)	65 (164-167, EtOH)		A
k	SO_2Me	75	25 (243-244, AcOH)	75 (178-179, AcOH)		A
l	CF_3	77	20 (154-155, hexane)	80 (138-139, hexane)		B
m	*t*-Bu	78		100 (96-99, EtOH)		C
n	NO_2	80		100 (193-194, EtOH)[d]		C

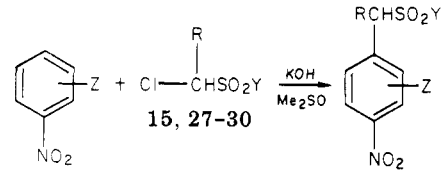
[a] Yields of isolated mixtures of products. [b] Determined by ^1H NMR signals of methylene protons. [c] **25e** was not isolated in the pure state. [d] Z = NO_2, isomers **24** and **25** are identical.

hand, *p*-nitrophenolate anion, in which the negative charge is conjugated directly with the nitro group, is unable to add the carbanion, and *p*-nitrophenol does not react with **1**.

Replacement of hydrogen in ortho-substituted nitrobenzenes can occur at both the para and ortho positions, giving two isomeric products **21** and **22** (Table III). Differentiation of **21** and **22** was based on comparison of ^1H NMR spectra of each pair of isomers. In the aromatic region the signals of the proton ortho to the nitro group coupled with the neighboring proton ($J \sim 8$ Hz) are present for **21** but not for **22**. We also observed that in ^1H NMR spectra measured in $CDCl_3$ signals of the methylene protons of ortho isomers of nitrobenzylic sulfones appear at lower field than those of the corresponding para isomers. This observation is valid, with a few exceptions, for spectra taken in other solvents. The ratio of para to ortho substitution is much higher than in nitrobenzene itself, owing to the statistical factor and to the somewhat hindered accessibility of the other ortho position. As with para-substituted nitrobenzenes, electron-donating and electron-withdrawing substituents do not interfere with the course of the reaction. In *o*-chloronitrobenzene and *o*-nitroanisole replacement of hydrogen para and ortho to the nitro group takes place exclusively, and replacement of Cl or RO is not observed. Addition of 1^- to *o*-(*tert*-butyl)nitrobenzene (**20h**) is strongly hindered by the secondary steric effect of the *tert*-butyl group in the formation of a σ complex, and the reaction does not proceed.

In reactions with meta-substituted nitrobenzenes, three isomeric products can be formed: para (**24**), ortho (**25**), and ortho' (**26**) (Table IV). Differentiation of the isomeric products was made in the same way as for **21** and **22**. In ^1H NMR spectra of **24a–m** signals due to two protons

Table V. Reactions of Nitroarenes with Tertiary Carbanions



3,20a,23n 31-35

nitro compd	Z	α-chloro sulfone	R	Y	product	yield,[a] %	mp, °C (solvent)	procedure
23n	3-NO_2	15	Ph	Ph	31	52	143-144 (MeOH)	C
3	H	27	n-C_4H_9		32	52	86-88.5 (MeOH)	A
20a	2-Cl	28	n-C_3H_7		33	46	101-102 (hexane, C_6H_6)	A
3	H	29	Ph		34	62	169-171 (AcOH)	C
23n	3-NO_2	30	Cl		35	81	133-135 (EtOH)	C

[a] Yields of isolated products.

ortho to the nitro group appear, whereas in those of **25a–m** and **26a–e** such signals are due to one proton. Signals of the methylene protons are also diagnostic; for each series **24**, **25**, and **26** these signals appear at higher, intermediate, and lower field, respectively. Only when Z = SO_2Me is this order reversed (**24k**, δ 5.38; **25k**, δ 5.24); however, these compounds were insoluble in $CDCl_3$, and the spectra were taken in Me_2SO-d_6 (Table V). Compound **25k** was identical with an authentic sample prepared by reaction of 2-nitro-4-(methylsulfonyl)benzyl chloride with sodium benzenesulfinate.

The overall yields of products from meta-substituted nitrobenzenes were good. The orientation pattern of substitution, which is governed by interplay between electronic and steric effects, is complicated and not easy to interpret. All three isomers were formed, with the ratio of para:(ortho + ortho') shown in parentheses, from the compounds in which Z = CH_3 (4.0), Cl (2.3), Br (1.4), OCH_3 (2.0), and F (1.1). For the first three, the less hindered ortho isomer prodominated over the more hindered ortho' isomer, whereas the ratios of ortho':ortho for Z = OCH_3 and F were 2.0 and 3.8, respectively. The significant reaction at the sterically hindered ortho' position of **23d,e** can be interpreted by taking into account that OCH_3 and F substituents exert electron-withdrawing inductive and electron-donating mesomeric effects, favoring nucleophilic attack on the neighboring positions more than on the conjugated remote position. This effect is less pronounced for Cl, Br, and I, and the sizes of these substituents (as well as OPh) hinder or prevent the reaction at the more sterically demanding ortho' position. The orientation pattern for strong electron-withdrawing substituents (**23j,k,l**)—preferential formation of the ortho over the para isomer—cannot yet be rationalized satisfactorily.

This interpretation of the orientation pattern based on the influence of substituents is obviously oversimplified. Since the reaction proceeds by a multistep process and the formation of the σ complex is reversible, it is possible that the rate of the second step, namely elimination of HCl from the σ complex, may also influence or even govern the orientation pattern. We do not yet have reliable evidence on the interdependence between the rate of the second step of vicarious substitution and structural features of the reactants. This problem is now under study.

Finally, Table V gives results of the vicarious substitution of hydrogen in nitrobenzene, *o*-chloronitrobenzene and *m*-dinitrobenzene with tertiary carbanions derived from several α-chloro sulfonyl compounds. These tertiary carbanions replace hydrogen exclusively in the position para to the nitro group.

Conclusion

The vicarious nucleophilic substitution of hydrogen in substituted nitroarenes can be accomplished by reaction with carbanions of α-haloalkyl phenyl sulfones and *N,N*-dialkyl-α-haloalkanesulfonamides. The reaction offers a simple and efficient method for introduction of α-functionalized alkyl substituents into an aromatic ring para or ortho to the nitro group.[21] The scope of this process and its general features are discussed in our recent general paper.[40] The synthetic applications and mechanistic problems of this reaction are currently under investigation.

Experimental Section

All melting points are uncorrected. Proton magnetic resonance (^1H NMR) spectra were recorded on either a JEOL INM-4H-100 or a Tesla 80 MHz BS 487 C spectrometer. GLC analysis was performed on a chromatron GCHF 18.3 instrument equipped with 1.25-m stainless steel column packed with 5% OV-17 on 100 Chromosorb W. For column chromatography silica gel Merck 230–400 mesh was used. TLC analyses were made on foil plates Merck 60F254, developed by spraying with MeOH–Me_2SO (10:1) saturated solution of KOH. All products formed strongly colored spots, those from the *p*-nitrobenzyl sulfones being red and those from the corresponding ortho isomers being blue. All new compounds had NMR spectra consisted with the structures and gave satisfactory C, H, and N microanalyses.

Materials. Commercially available aromatic nitro compounds were purified when necessary. The following nitrocompounds were prepared according to known methods: *N,N*-dimethyl-4-nitroaniline (**8b**),[22] 1-(*tert*-butyl)-4-nitrobenzene (**8f**),[23] 2-(4-nitrophenyl)-1,3-dioxolane (**8g**),[24] 4-nitrobiphenyl (**8h**),[25] 4-nitrophenyl methyl sulfide (**8i**),[26] 1-(trifluoromethyl)-4-nitrobenzene (**8o**),[27] 4-nitrophenyl methyl sulfone (**8p**),[26] *N,N*-di-

(21) A valuable method for the introduction of alkyl substituents into some nitroarene molecules via reaction with alkylmagnesium halides was recently reported: Bartoli, G.; Rosini, G. *Synthesis* **1976**, 270. Bartoli, G.; Leardini, R.; Lelli, M.; Rosini, G. *J. Chem. Soc., Perkin Trans. 1* **1977**, 884.

(22) Fitch, H. M. *Org. Synth.* **1947**, *27*, 62.

(23) Shoesmith, J. B.; Mackie, A. *J. Chem. Soc.* **1928**, 2334.

(24) Hibbert, H.; Sturrock, J. G. *J. Am. Chem. Soc.* **1928**, *50*, 3374.

(25) Schultz, G. *Liebigs Ann. Chem.* **1874**, *174*, 201.

(26) Oxley, P.; Partridge, M. W.; Robson, T. D.; Short, W. F. *J. Chem. Soc.* **1946**, 763.

methyl-2-nitroaniline (**20b**),[28] 2-nitrophenyl phenyl ether (**20d**),[29] 1-(*tert*-butyl)-2-nitrobenzene (**20h**),[23] *N,N*-dimethyl-3-nitroaniline (**23f**),[22] 3-nitrophenyl phenyl ether (**23g**),[29] 2-(3-nitrophenyl)-1,3-dioxolane (**23i**),[30] 3-nitrophenyl methyl sulfone (**23k**),[31] 1-(*tert*-butyl)-3-nitrobenzene (**23m**).[23] α-Halo sulfonyl compounds: chloromethyl 4-morpholinyl sulfone (**2**),[32] fluoromethyl phenyl sulfone (**11**),[33] iodomethyl phenyl sulfone (**13**),[34] α-chlorobenzyl phenyl sulfone (**15**),[35] dichloromethyl phenyl sulfone (**16**),[36] 1-chloropropyl phenyl sulfone (**14**),[37] 1-chlorobutyl 4-morpholinyl (**28**),[37] 1-chloropentyl 4-morpholinyl sulfone (**27**),[37] α-chlorobenzyl 4-morpholinyl sulfone (**29**),[37] *N*-methyl-*N*-phenyldichloromethanesulfonamide (**30**).[37]

Chloromethyl Phenyl Sulfone (1). Sodium benzenesulfinate dihydrate (20 g, 0.1 mol) and chlorobromomethane (15.5 g, 0.12 mol) in Me_2SO (50 mL) were heated on a water bath for 4 h. The mixture was cooled, poured into water, and extracted with dichloromethane (3 × 100 mL). The combined extracts were washed with water and dried with $MgSO_4$. Evaporation of the solvent and recrystallization from CCl_4 gave chloromethyl phenyl sulfone (**1**): 11.2 g (59%); mp 52 °C (lit.[38] mp 51–52.5 °C).

Bromomethyl Phenyl Sulfone (12). Bromomethyl phenyl sulfone was prepared as described above using dibromomethane (21 g) instead of chlorobromomethane: yield 12.6 g (54%); mp 50–51 °C (CCl_4) (lit.[39] mp 50–52 °C).

Reaction of Nitroarenes with α-Halo Sulfonyl Compounds. General Procedure. Procedure A. To a stirred solution of nitroarene (0.01 mol) and 1-chloroalkyl phenyl sulfone or 1-chloroalkyl 4-morpholinyl sulfone (0.01 mol) in Me_2SO (15 mL) was added powdered KOH (4 g) and the reaction carried out at room temperature for 1 h. The mixture was poured into 2% HCl (100 mL) and extracted with chloroform, and the extract was dried over $MgSO_4$. A small portion of the extract was examined by ^1H NMR or by GLC to estimate the proportion of isomers in the crude mixture. The combined extracts were evaporated and the products were isolated and separated by column chromatography using chloroform as eluent. The products were purified by recrystallization.

Procedure B. Reaction and workup were completed as in procedure A. After evaporation of the solvent one isomer was isolated by recrystallization. The combined mother liquors were evaporated and other isomers were isolated by column chromatography.

Procedure C. Reaction and workup were completed as in procedure A. After evaporation of the solvent the crude product was purified by recrystallization (This procedure was used when only one isomer was formed).

Procedure D. Nitroarene (0.01 mol) and 1-chloroalkyl aryl sulfone (0.01 mol) dissolved in THF (15 mL) were added dropwise into a stirred mixture of powdered KOH (4 g) and liquid ammonia (30 mL) at −30 °C over 15 min. The reaction was carried out for 1 h and the ammonia then evaporated. The residue was diluted with water, acidified with hydrochloric acid, and worked up as in Procedure A.

Reaction of Nitrobenzene with 2. Reaction by procedure A gave 4-nitrobenzyl 4-morpholinyl sulfone (**5**), mp 168–169 °C (AcOH), and 2-nitrobenzyl 4-morpholinyl sulfone (**7**), mp 143–144 °C (EtOH) in a total yield of 53%; ratio **5**:**7** = 35:65.

Reaction of 4-Chloronitrobenzene with 2. Reaction by procedure C gave 5-chloro-2-nitrobenzyl 4-morpholinyl sulfone (**10a**): yield 75%; mp 172–173 °C (AcOH).

Reaction of Nitrobenzene with Halomethyl Phenyl Sulfones (Table I). A solution of halomethyl phenyl sulfone (20 mmol) and nitrobenzene (20 mmol) in Me_2SO (5 mL) was added dropwise to a suspension of powdered KOH (2 g) in Me_2SO (10 mL) with stirring at 20 °C. The mixture was stirred for 1 h, diluted with water, acidified with HCl, and extracted with chloroform (3 × 50 mL). The ratio of isomers 4:6 was determined by GLC.

Reactions of Nitrobenzene with Tertiary CH Acids (Table I). Reactions were carried out by procedure A. ^1H NMR spectra (methine group proton shift) of the crude mixture indicated only one product. **17**, mp 104–105.5 °C (EtOH), **18**, mp 116–117.5 °C (EtOH), and **19**, mp 169–170 °C (AcOH) (lit.[35] mp 170–171 °C). GLC analysis of crude mixtures from the reaction **3** with **14** showed an absence of the ortho isomer of 1-(*o*-nitrophenyl)propyl phenyl sulfone.

^1H NMR Data of Products 5–35.[41a] **4**: 4.72 (s, 2), 7.4–7.8 (m, 7), 8.22 (d, 2, J = 9.5). **6**: 4.97 (s, 2), 7.4–8.2 (m, 9). **5**: 3.0–3.2 (m, 4), 3.5–3.7 (m, 4), 4.25 (s, 2), 8.0–8.3 (m, 4). **7**: 3.1–3.25 (m, 4), 3.6–3.75 (m, 4), 4.71 (s, 2), 7.4–7.6 (m, 3), 7.9–8.1 (m, 1). **9a**:[41b] 5.05 (s, 2), 7.4–7.8 (m, 7), 8.12 (d, 1, J = 9). **9b**:[41c] 3.58 (s, 6), 5.29 (s, 2), 7.6–8.2 (m, 6) 8.41 (d, J = 10). **9c**:[41d] 3.8 (s, 3), 5.21 (s, 2), 6.8 (d, 1, J = 2.7), 7.1 (dd, 1, J = 2.7, J = 9.8), 7.6 (s, 5), 8.1 (d, 1, J = 9.8). **9d**: 5.0 (s, 2), 7.0–7.8 (m, 12), 8.10 (d, 1, J = 8). **9e**: 1.14 (t, 3, J = 7), 2.51 (q, 2, J = 7), 4.85 (s, 2), 7.0–7.7 (m, 7), 7.80 (d, 1, J = 8). **9f**: 2.48 (s, 9), 4.90 (s, 2), 7.1–7.65 (m, 7), 7.84 (d, 1, J = 9). **9g**: 3.9 (m, 4), 4.61 (m, 1), 5.1 (s, 2), 7.5–8.4 (m, 8). **9h**: 5.11 (s, 2), 7.8–8.3 (m, 13). **9i**:[41c] 2.45 (s, 3), 5.21 (s, 2), 7.1–8.1 (m, 8). **9j**: 4.92 (s, 2), 7.45–8.25 (m, 8). **9k**: 4.91 (s, 2), 7.5–8.0 (m, 8). **9l**: 4.89 (s, 2), 7.1–8.1 (m, 8). **9m**: 4.97 (s, 2), 7.45–7.8 (m, 5), 8.1–8.65 (m, 3). **9n**: 5.08 (s, 2), 7.5–8.6 (m, 8). **9o**: 4.98 (s, 2), 7.5–8.3 (m, 8). **9p**:[41d] 3.21 (s, 3), 5.28 (s, 2), 7.5–8.0 (m, 6), 8.2–8.45 (m, 2). **9r**:[41d] 5.25 (s, 2), 7.4–8.31 (m, 8). **10a**: 3.1 (m, 4), 3.3–3.5 (m, 4), 4.71 (s, 2), 7.5–8.1 (m, 3). **17**: 0.7–0.91 (m, 3), 2.0–2.75 (m, 2), 4.13 (dd, 1, J = 4, J = 11), 7.1–7.5 (m, 5), 7.61 (d, 2, J = 8), 8.12 (d, 2, J = 8). **18**: 5.49 (s, 1), 7.3–8.2 (m, 14). **19**: 5.81 (s, 1), 7.5–7.9 (m, 7), 8.33 (d, 2, J = 8). **21a**:[41e] 4.85 (s, 2), 7.37 (dd, 1, J = 2, J = 8.5), 7.45–7.85 (m, 6), 7.98 (d, 1, J = 8.5). **21b**: 2.76 (s, 6), 4.25 (s, 2), 6.45 (dd, 1, J = 2, J = 10), 6.65 (d, 1, J = 2), 7.3–7.8 (m, 6). **21c**: 3.80 (s, 3), 4.30 (s, 2), 6.64 (dd, 1, J = 2, J = 8), 6.85 (d, 1, J = 2), 7.3–7.8 (m, 6). **21d**: 4.21 (s, 2), 6.51 (d, 1, J = 2), 6.75–7.75 (m, 11), 7.80 (d, 1, J = 8). **21e**: 2.50 (s, 3), 4.30 (s, 2), 7.01 (d, 1, J = 8), 7.06 (s, 1), 7.3–7.7 (m, 5), 7.80 (d, 1, J = 8). **21f**:[41e] 5.00 (s, 2), 7.5–7.85 (m, 7), 8.12 (d, 1, J = 7.5). **21g**:[41e] 4.97 (s, 2), 7.5–7.85 (m, 6), 7.97 (d, 1, J = 2), 8.17 (d, 1, J = 8). **22a**:[41e] 4.80 (s, 2), 7.3–7.85 (m, 8). **22b**: 2.71 (s, 6), 4.37 (s, 2), 6.9–7.1 (m, 2), 7.3–7.75 (m, 6). **22c**: 3.84 (s, 3), 4.37 (s, 2), 6.95–7.75 (m, 8). **22d**: 4.45 (s, 2), 6.85–7.0 (m, 4), 7.1–7.75 (m, 9). **22f**:[41e] 4.85 (s, 2), 7.5–8.25 (m, 8). **24a**: 2.21 (s, 3), 4.40 (s, 2), 7.16 (d, 1, J = 8), 7.35–7.65 (m, 5), 7.87 (d, 1, J = 8), 7.94 (s, 1). **24b**: 4.59 (s, 2), 7.40–7.75 (m, 6), 8.0–8.15 (m, 2). **24c**: 4.76 (s, 2), 7.5–7.9 (m, 6), 8.26 (dd, J = 1, J = 7), 8.41 (d, 1, J = 1). **24d**: 3.44 (s, 3), 4.46 (s, 2), 7.3–7.7 (m, 7), 7.77 (dd, 1, J = 2, J = 9). **24e**: 4.55 (s, 2), 7.5–8.2 (s, 8). **24f**:[41c] 3.79 (s, 6), 5.14 (s, 2), 7.36 (d, 1, J = 7), 7.65–8.1 (m, 6), 8.60 (dd, 1, J = 1, J = 7). **24g**: 4.22 (s, 2), 6.62 (d, 1, J = 1.5), 6.8–7.65 (m, 11), 7.80 (d, 1, J = 8.5). **24h**: 4.64 (s, 2), 7.45–7.75 (m, 6), 8.15 (dd, 1, J = 2, J = 8.5), 8.51 (d, 1, J = 2). **24i**: 3.97 (s, 4), 4.69 (s, 2), 5.88 (s, 1), 7.27 (d, 1, J = 8.5), 7.4–7.8 (m, 5), 8.03 (dd, J = 2.5, J = 8.5), 8.38 (d, 1, J = 2.5). **24j**:[41e] 5.00 (s, 2), 7.49–7.94 (m, 6), 8.49 (dd, 1, J = 2, J = 8), 8.66 (d, 1, J = 2). **24k**:[41d] 3.41 (s, 3), 5.38 (s, 2), 7.5–7.95 (m, 6), 8.54 (dd, J = 1, J = 9), 8.70 (d, 1, J = 1). **24l**: 4.7 (s, 2), 7.5–7.9 (m, 5), 8.1 (d, 1, J = 8.5), 8.65–8.85 (m, 2). **24n**:[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). **25a**: 2.36 (s, 3), 4.82 (s, 2), 7.2–7.95 (m, 8). **25b**: 4.81 (s, 2), 7.35–7.81 (m, 7), 7.95 (s, 1). **25c**: 4.95 (s, 2), 7.3–8.0 (m, 7), 8.18 (s, 1). **25d**: 3.80 (s, 3), 4.80 (s, 2), 7.0–7.8 (m, 8). **25e**: 5.00 (s, 2), 7.4–7.9 (m, 8). **25f**:[41c] 3.64 (s, 6), 5.31 (s, 2), 7.6–8.3 (m, 7), 8.60 (d, 1, J = 2, 5). **25g**: 4.45 (s, 2), 6.85–7.0

(27) Burmakov, A. I.; Alekseeva, L. A.; Yagupolskii, L. M. *Zh. Org. Khim.* **1972**, *8*, 153.
(28) Hodgson, H. H.; Kershaw, A. *J. Chem. Soc.* **1930**, 277.
(29) Lock, G. *Monatsh. Chem.* **1930**, *55*, 167.
(30) Indictor, N.; Horodniak, J. W.; Jaffe, H.; Miller, D. *J. Chem. Engl. Data* **1969**, *14*, 76.
(31) Twist, R. F.; Smiles, S. *J. Chem. Soc.* **1925**, *127*, 1249.
(32) Christensen, L. W.; Seaman, J. M.; Truce, W. E. *J. Org. Chem.* **1973**, *38*, 2243.
(33) Yagupolskii, L. M.; Aleksandrov, A. M. *Zh. Obshch. Khim.* **1968**, *38*, 1503.
(34) Jończyk, A.; Pytlewski, T. *Synthesis* **1978**, 883.
(35) Jarvis, B. B.; Sankaitis, J. C. *J. Am. Chem. Soc.* **1973**, *95*, 7708.
(36) Middelbos, W.; Strating, J.; Zwanenburg, B. *Tetrahedron Lett.* **1971**, 351.
(37) Goliński, J.; Mąkosza, M. *Synthesis* **1979**, 823.
(38) Eckstein, Z.; Polubiec, E.; Palut, D. *Przem. Chem.* **1968**, *47*, 544.
(39) Bordwell, F. G.; Hoyt, E. B.; Jarvis, B. B.; Williams, J. M. *J. Org. Chem.* **1968**, *33*, 2030.
(40) Mąkosza, M. In "Current Trends in Organic Synthesis"; Nozaki, H., Ed.; Pergamon Press: Oxford, 1983; p 401.

(41) (a) Unless otherwise stated the spectra were taken in $CDCl_3$. (b) In $(CD_3)_2CO$. (c) In CF_3COOH. (d) In Me_2SO-d_6. (e) In a 1:1 mixture of $(CD_3)_2CO$ and Me_2SO-d_6.

(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]

Mieczysław Makosza* and Jerzy Winiarski

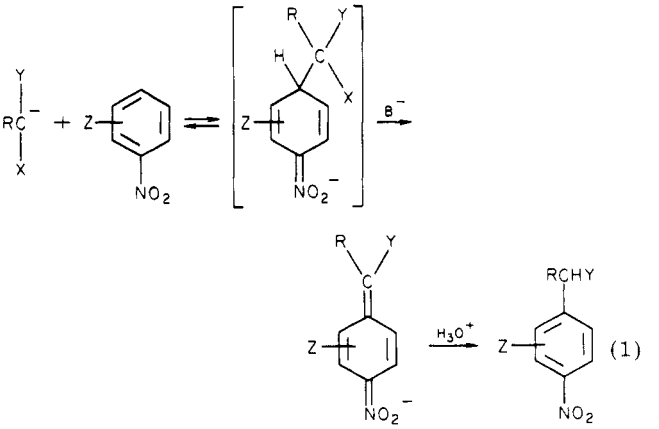
Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland, and Department of Chemistry, Technical University (Politechnika), Warsaw, Poland

Received April 4, 1983

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*.

0022-3263/84/1949-1494$01.50/0