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Introduction of a carbon–carbon bond into electron-deficient aromatic compounds

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ABSTRACT. Methods for introducing a new carbon–carbon bond into aromatic compounds containing such electron-accepting groups as NO_2, SO_2CF_3, or oxazoline and into perfluoroarenes are discussed in the review. These methods comprise S_NAr reactions, oxidation of anionic σ-complexes, isolated previously or obtained *in situ*, and vicarious nucleophilic substitution reactions.

The bibliography contains 371 references.

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I. Introduction

The interest of organic chemists in nucleophilic aromatic substitution, and in anionic σ-complexes as possible intermediates in these reactions, has not weakened during almost four decades. Both the overall number of publications and the continuous appearance of new reviews and monographs indicate this.[1–20] In spite of apparent outward simplicity the nucleophilic aromatic substitution reaction is distinguished by the complexity and diversity of its mechanisms.

Reactions of the S_NAr type which lead to the formation of a new C–C bond have special significance and are consequently extremely important in organic synthesis. Such reactions occur most smoothly with perfluoroarenes. However for several halonitroarenes they proceed in a far more complex manner and frequently lead to mixtures of products. The functionalisation of nitroarenes has great importance since the compounds obtained serve as starting materials for the synthesis of various biologically active heterocycles.[21,22]

It is well known that at first a rapid and reversible formation of anionic σ-complexes occurs at an unsubstituted carbon atom in the reaction of charged nucleophiles with electron-deficient arenes. The most stable of these are complexes with carbon–carbon bonds since their rearrangement into 1,1-σ-complexes, from which substitution products are then formed, proceeds most slowly. As a result they are able to undergo various conversions such as entering into oxidation-reduction reactions with the participation of the nitro group. These complexes may also be oxidised by suitable oxidising agents so that halogens and other substituents in the benzene ring are unaffected. Thus the preparation of anionic σ-complexes and their subsequent oxidation may be an alternative method of introducing a C–C bond into an electron-deficient arene. It is probable that this very route is the most acceptable for substrates containing several electron-accepting groups such as 1,3,5-trinitrobenzene or 1,3,5-*tris*-(trifluoromethylsulphonyl)benzene which form stable σ-complexes. However good results were also obtained when oxidising unstable σ-complexes formed from mononitroarenes.

Arenes activated by an oxazoline group, besides nitro- and *tris*-(trifluoromethylsulphonyl)-aromatic compounds, are widely used at present as substrates in S_NAr type reactions. Although the activating effect of this group is weaker than that of a NO_2 group similar compounds prove to be valuable intermediates in synthesis.

Methods are discussed in the present review for introducing a C–C bond into electron-deficient arenes and include nucleophilic substitution of halogen and hydrogen. Since there are practically no data on reactions of the S_NAr type with carbanions in the known reviews[1–5] and monograph[6] they are considered in ample detail in the present review. On the other hand a whole series of reviews[7–19] and a recently published fundamental monograph[20] have been devoted to anionic σ-complexes and contain information on complexes with various types of C–Nu bonds, and on their physicochemical characteristics and stability constants. Consequently we will not list all the σ-complexes with C–C bonds obtained to date in the present review but will indicate only the main carbanions with which σ-complexes are successfully obtained. Principal attention will be paid to the conditions for obtaining σ-complexes and also to the methods for aromatising them.

Reactions for adding organometallic compounds and carbanions to mononitroarenes are segregated into a separate section. Removal of hydride ion from an intermediate unstable σ-complex occurs only under the action of an external oxidising agent or a nitroarene. The interesting vicarious nucleophilic substitution reactions are included here.

The limited size of the review does not permit inclusion of S_NAr type reactions (and the formation of σ-complexes) in neutral and cationic complexes of arenes with the transition metals, which are being widely studied at present. Reactions with carbanions in the heterocyclic series have been partially considered in reviews which have appeared comparatively recently.[23,24]

II. Nucleophilic aromatic substitution reactions

1. Substrates activated by NO_2, SO_2CF_3 and oxazoline groups

a) Substitution of halogen

As mentioned above halonitro derivatives are the most frequently used subjects of nucleophilic aromatic substitution reactions since the nitro group is one of the very strong electron-accepting substituents

Table 1. Replacement of halogen in halonitrobenzenes by carbanions of malonic, acetoacetic and cyanoacetic esters and of acetylacetone.

No.	Substrate	Carbanion from	Group replaced	Solvent	Yield, %	Refs.
1	1-Chloro-2-nitrobenzene	$NaCH(COOEt)_2$	Cl	t-BuOH	54	[32]
2	1-Bromo-2-nitrobenzene	$NaCH(COOEt)_2$	Br	Et_2O		[31]
3	4-Bromo-3-nitrobenzonitrile	$NaCH(COOEt)_2$	Br	Et_2O		[31]
4	1,3-Dichloro-2-nitrobenzene	$NaCH(COOEt)_2$	Cl	t-BuOH	84	[32]
5	1-Chloro-2,4-dinitrobenzene	$NaCH(COOEt)_2$	Cl	EtOH		[30]
6	1-Bromo-2,4-dinitrobenzene	$NaCH(COOEt)_2$	Br	EtOH		[33, 35]
7	1-Chloro-2,6-dinitrobenzene	$NaCH(COOEt)_2$	Cl	Et_2O		[25]
8	1-Chloro-4-methyl-2,6-dinitrobenzene	$NaCH(COOEt)_2$	Cl	Et_2O		[27]
9	1,5-dichloro-2,4-dinitrobenzene	$NaCH(COOEt)_2$	Cl	Et_2O		[28]
10	1-Chloro-2,4,6-trinitrobenzene	$NaCH(COOEt)_2$	Cl	$EtOH+C_6H_6$		[29]
11	1-Chloro-2,4-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	75	[37]
		NaCH(COOEt)COMe	Cl	Et_2O	74	[45]
		NaCH(COOEt)COMe	Cl	EtOH		[30, 36]
12	1-Chloro-2,6-dinitrobenzene	NaCH(COOEt)COMe	Cl	EtOH	90	[26]
13	1,2-Dichloro-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	59	[41]
14	1-Bromo-2-chloro-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	88	[38]
15	1-Chloro-2-iodo-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	57,4	[40]
16	1,4-Dichloro-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	56	[42]
17	1-Bromo-4-chloro-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	98	[39]
18	1-Chloro-4-iodo-3,5-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	84	[43]
19	1,5-dichloro-2,4-dinitrobenzene	NaCH(COOEt)COMe	Cl	Et_2O	80	[30]
20	1-Chloro-2,4,6-trinitrobenzene	NaCH(COOEt)COMe	Cl	EtOH		[44]
21	1-Chloro-2-nitrobenzene	NaCH(CN)COOEt	Cl	t-BuOH	70	[43]
22	1-Chloro-4-nitrobenzene	NaCH(CN)COOEt	Cl	EtOH		[46]
23	1-Chloro-2,4-dinitrobenzene	NaCH(CN)COOEt	Cl	EtOH	90	[46]
24	2-Chloro-5-nitrobenzonitrile	NaCH(CN)COOEt	Cl	EtOH		[30]
25	1-Chloro-2,4,6-trinitrobenzene	NaCH(CN)COOEt	Cl	EtOH	53	[46]
26	1-Chloro-2,4-dinitrobenzene	$NaCH(COMe)_2$	Cl	EtOH	54	[47, 48]

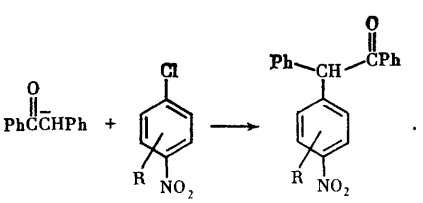
and halogen is a good leaving group. The activating influence of other electron-accepting groups (CN, CF_3, COR, etc.) for substitution of halogen in ArX usually proves to be insufficient.

The substitution of halogen under the action of anions of malonic,[25–33] acetoacetic[26,30,34–35] and cyanoacetic[30,43,46] esters and acetylacetone[47,48] in ether and alcohol has been studied recently. In these solvents carbanions display fairly low reactivity, they react successfully with strongly activated di- and trinitrohalobenzenes where yields are satisfactorily high (Table 1).

For example the sodium salts of malonic and acetoacetic esters do not react in alcohol with 2-chloro-5-nitrobenzonitrile† or with 2-chloro-5-nitrobenzoic acid.[30] However in t-butanol the potassium salts of cyanoacetic and malonic esters react successfully with *o*-chloronitrobenzene and give low yields of substitution products in ether and ethanol.[32] Generally speaking these studies are fairly complex to analyse since product yields are often not given. It is interesting to mention that the structures of the α-picryl and 2,4-dinitrophenyl derivatives of acetoacetic ester, obtained at the end of the past century,[44] were established only comparatively recently. It was shown that they were enols not only in solution[45,49,50] but also in the solid state.[51] α-Picrylacetylacetone is completely enolised in solution.[52]

The new stage in the study of nucleophilic aromatic substitution is linked with the use of dipolar aprotic solvents of the type of dimethylsulphoxide (DMSO), hexamethylphosphoramide (HMPA) or pyridine (Py) which usually smooth the course of the reaction. Thus the sodium salts of malonic ester and acetylacetone react with *o*-chloronitrobenzene, *p*-chloronitrobenzene, and 1,4-dichloro-2-nitrobenzene in dimethylformamide (DMF), DMSO and HMPA at 100 °C in 1 to 5 h, the yields of arylation products being from 20 to 65%.[53] Arylation of phenylacetonitrile with *p*-chloronitrobenzene was carried out successfully in pyridine in the presence of KOH.[54]

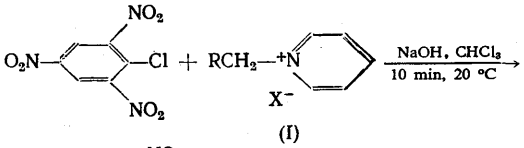
Arylation of the carbanion of desoxybenzoin by various halonitrobenzenes was carried out in DMSO and DMF, *p*-halonitrobenzenes gave products in ~60% yield but *ortho* isomers reacted non-selectively and yields of substitution products were low.[55]



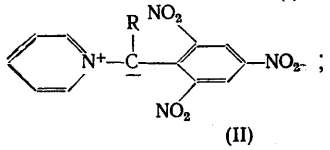
In aromatic nitrotoluenes the methyl group located in the *para* position to the nitro group may be deprotonated under the action of base. It was shown that 2,4,6-trinitrotoluene reacts in the presence of MeONa with picryl chloride, 1-chloro-2,4-dinitrobenzene, 1-fluoro-2,4-dinitrobenzene and 1,3-dibromo-2,4,6-trinitrobenzene with the formation of polynitrodiphenylmethanes.[56] Highest yields of products were achieved on carrying out the reaction in a tetrahydrofuran (THF)–DMSO mixture however even under these conditions 2,4,6-trinitrotoluene did not react with mononitro- and 1-halo-3,5-dinitro- and 1-halo-2,6-dinitrobenzenes.[56]

† A report on the isolation of a product from the reaction of sodiomalonic ester with 4-bromo-3-nitrobenzonitrile is seemingly erroneous.[32,30]

Among the other reactions of halonitrobenzenes with carbanions it is necessary to mention the preparation of ylids (II) by reacting picryl chloride with quaternary salts of pyridine (I) in the presence of alkali.[57]



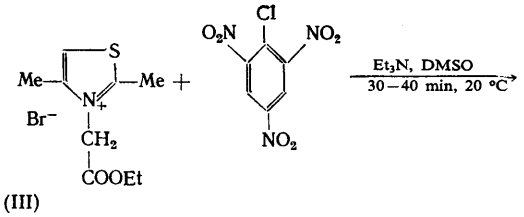
(I)



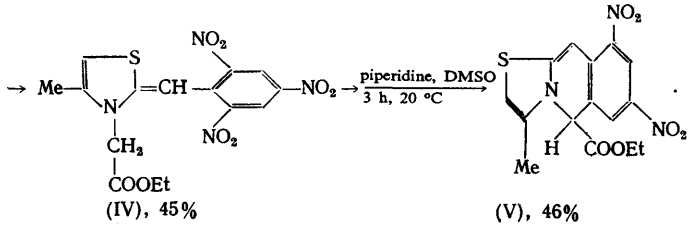
(II)

R = PhCO, MeCO etc.

Reactions of picryl chloride with salts of type (III) in DMSO in the presence of base lead to the formation either of ylid (IV) or the product of intramolecular substitution (V) of a nitro group by the carbanion of ylid (IV).[58]

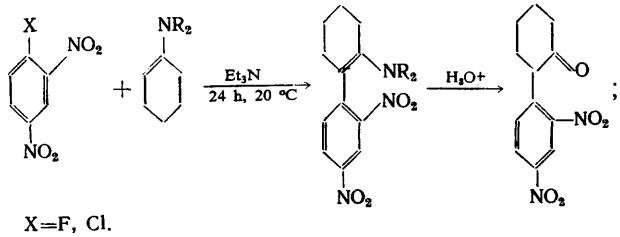


(III)



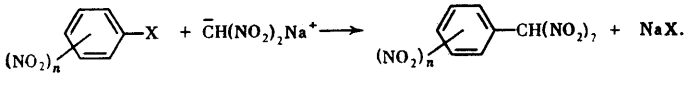
(IV), 45% (V), 46%

Products of substitution of the halogen atom in 1-chloro-2,4-dinitrobenzene or 1-fluoro-2,4-dinitrobenzene by enamines were obtained in 80–90% yield in the presence of an equimolar quantity of triethylamine.[59] It was noted that in the absence of Et_3N yields were sharply reduced (to 6–30%).



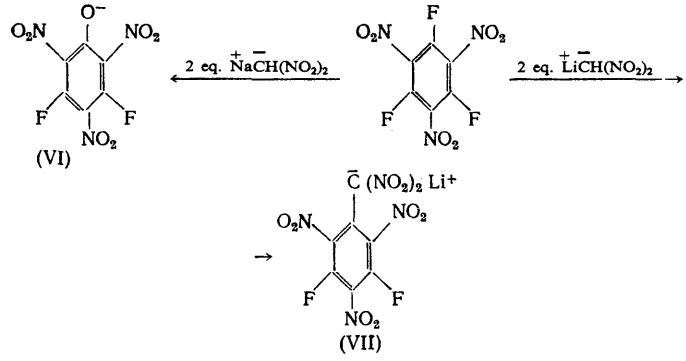
X=F, Cl.

Reactions of the sodium salt of dinitromethane with various halonitrobenzenes in DMF have been investigated.[60]



1-Halo-2,4-dinitrobenzenes displayed the greatest reactivity in this reaction. The reaction of 1,2-dichloro-4-nitrobenzene and 1,4-dichloro-3-nitrobenzene with $\bar{C}H(NO_2)_2Na^+$ was not complete even after a year (20 to 25 °C); *o*- and *p*-chloronitrobenzenes and 2,3,5,6-tetrachloro-3-nitrobenzene generally did not react.

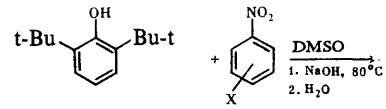
2,4-Dinitrophenoxide and picrate were isolated on attempting to react the sodium salts of bromodinitromethane and trinitromethane with 1-chloro-2,4-dinitro- and 1-chloro-2,4,6-trinitrobenzenes respectively.[60] The picrate (VI) was isolated from the reaction of 1,3,5-trifluorotrinitrobenzene with the Na salt of dinitromethane. However use of the Li salt made it possible to obtain the *C*-arylated product (VII) in 43% yield[61] (see also p. 755). Regrettably no opinion was expressed on possible routes of forming phenoxides and picrates.[60]

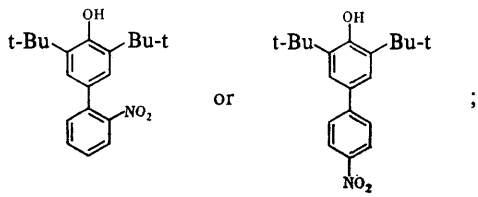


(VI)

(VII)

Phenoxide ions and aromatic amines occasionally emerge as *C*-nucleophiles in S_NAr type reactions[62–66] (see also p. 761). Usually 2,6-dialkylphenols react with *p*-chloronitrobenzene in DMSO in the presence of KOH giving diphenyl ethers.[62] However 2,6-di-(t-butyl)phenol forms *C*-arylation products under these conditions[62,63] (cf. p. 761).

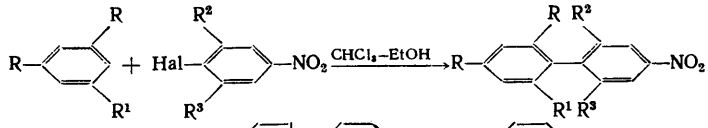




64–97%

X = 2-F, Cl, Br, I, NO_2, SO_2Ph, 4-NO_2.

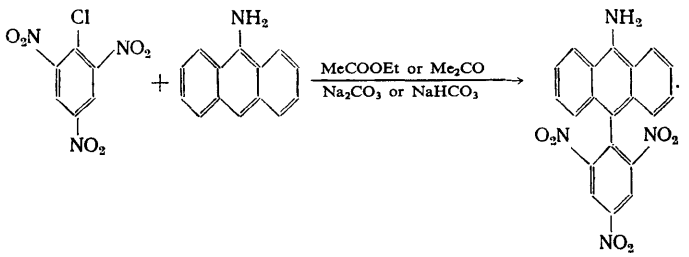
Diaryls formed by reaction of aminobenzenes with activated aryl halides are intensely coloured and are intramolecular charge-transfer complexes.[65,66]



R, R^1 = N⟨ ⟩, N⟨ ⟩, NMe_2, N⟨ ⟩O;

Hal = F, Cl; R^2, R^3 = NO_2, H, CN, CO_2Me.

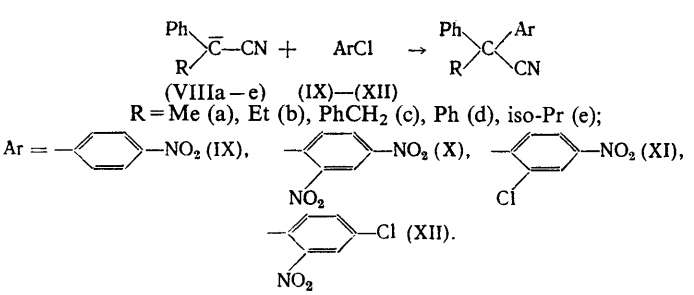
The reactivity of ArHal and arylamines in these reactions varies within wide limits. Thus the interaction of picryl chloride, the most reactive of all the aryl chlorides, with all triaminobenzenes proceeds readily, with dipyrrolidino- and dipiperidinobenzenes more extended heating is required and with mono(dialkylamino)benzenes generally does not occur.[65] Products of *C*-arylation were also obtained in the reaction of 9-aminoanthracene and 2-amino-*N*-methylindole with picryl chloride.[66]



It was noted that the remaining primary amines investigated (derivatives of benzene, diphenyl, naphthalene, pyridine, quinoline, carbazole, etc.) were arylated at nitrogen.[66]

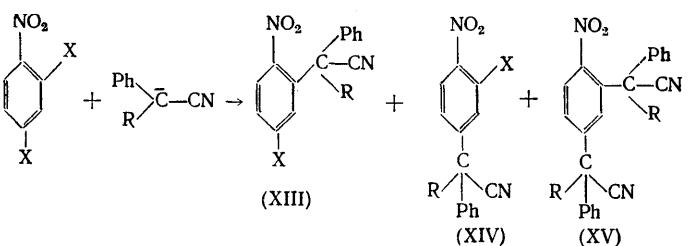
The application of dipolar aprotic solvents has therefore extended significantly the scope of the nucleophilic aromatic substitution reaction, however the high cost of these solvents and mainly the difficulties of separating the reaction products from them significantly limit their use. The application of phase-transfer catalysis (PTC) is more promising.[67–69] Good results were obtained on using PTC to prepare polynitrodiphenylmethanes from 2,4,6-trinitrotoluene and picryl chloride or 1-chloro-2,4-dinitrobenzene. Reaction was effected in methylene chloride in the presence of aqueous alkali solution and a phase transfer agent (18-crown-6 ether, $PhCH_2\overset{+}{N}Et_3Cl^-$), yields of products were ~90%.[70]

The PTC method has been successfully applied for the arylation of alkyl- and phenylacetonitriles with various chloronitrobenzenes in a system of 50% aqueous NaOH in the presence of triethylbenzylammonium chloride. Yields of products were 80–90%.[54,71–75]



Regrettably not all reactions proceed readily under these conditions. For example, in the case of carbanions (VIIId) and (VIIIe) the results varied with the nature of ArCl and the reaction conditions. Both carbanions form normal substitution products with chlorodinitrobenzene (X) however nitroarylation occurs only in the presence of DMSO with 1,2-dichloro-3-nitrobenzene (XI). In the absence of DMSO (VIIId) and (XI) react to form 1,1-dicyanotetraphenylethane and reduction products of the nitro group but 4-chloro-2-nitrophenol is formed from (VIIIe) and (XII) in the presence of DMSO.[54]

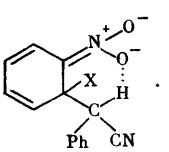
It was also noted that anions of active methylene compounds (phenylacetonitrile, desoxybenzoin, ethyl cyanoacetate, malonic ester) do not form arylation products under PTC conditions in good yield.[55,74,75] These reactions are successfully effected in aprotic dipolar solvents.[53–55] It is interesting that such carbanions replace the halogen in the *ortho* position of 2,4-dihalonitrobenzenes although the yield of product (XIII) was fairly low.[75] These reactions always give a complex mixture of products and are accompanied by resinification to a significant extent (see also pp. 768 and 769). However carbanions of phenylalkylacetonitriles and also ethyl malonate replace halogen predominantly at the *para* position.[75]



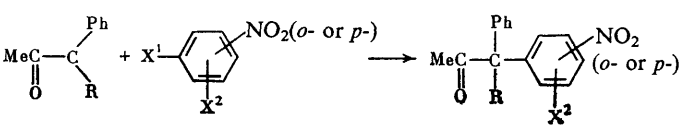
X = Cl, Br; R = Me, $PhCH_2$, Et, Ph, H.

The yield of product (XIV) was 70–90%, compounds (XIII) and (XV) if formed were in minimal amounts (2–4%). Compounds (XIII) and (XV) were obtained in somewhat larger yield from benzylphenylacetonitrile (15.6% and 10.7% respectively).

The observed phenomenon of the preferential replacement of the *ortho* halogen in 2,4-dihalonitrobenzenes is explained by the *ortho* effect of the nitro group which is also known for reactions with other nucleophiles. In the reaction of 1,3-dihalo-4-nitrobenzenes with tertiary amines and anionic reagents, the halogen atom in the *para* position is the more reactive while with primary and secondary amines the *ortho* halogen is more reactive.[3] It was suggested that the presence of hydrogen atoms in the anion enables the formation of an intramolecular hydrogen bond with the *ortho*-nitro group in the σ-anionic complex which leads to its further stabilisation and increases the rate of nucleophilic substitution of the halogen atom in the *ortho* position (see also Chapter IV, section 2).



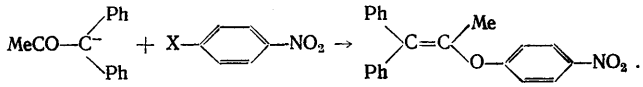
Nitroarylation of ketone enolates has been carried out in aprotic dipolar solvents and in a two-phase catalytic system.[76]



R=H, Et, Pr, Bu; X^1=F, Cl; X^2=H, Cl, NO_2.

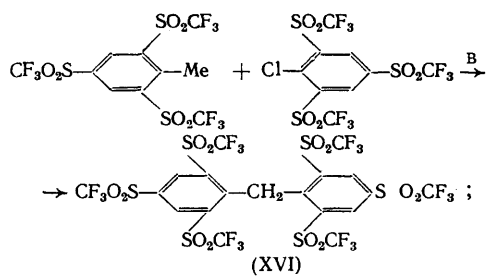
The reaction of benzylmethylacetone with halonitrobenzenes has been carried out in DMSO or DMF using NaOH or NaH. 1-Alkyl-1-phenylacetones are arylated better in a two-phase system, the reaction being accelerated by small additions of DMSO. Yields

were higher for *o*- and *p*-fluoronitrobenzenes than for the chloro derivatives. It was noted that only the product of *O*-arylation was isolated on arylation of 1,1-diphenylacetone under these conditions.[76]



It is evident from the material stated above that carrying out a nucleophilic substitution reaction under PTC conditions is promising. Regrettably it was impossible to react the most reactive nitroaromatic compounds of the picryl halide type with insufficiently stable carbanions under these conditions.

It is known that the SO_2CF_3 group displays an even stronger electron-accepting effect than the nitro group. Like 2,4,6-trinitrotoluene 1-methyl-2,4,6-*tris*-(trifluoromethylsulphonyl)benzene reacts readily in the presence of various bases (B) with 1-chloro-2,4,6-*tris*-(trifluoromethylsulphonyl)benzene with the formation of the corresponding diphenylmethane (XVI).[77]

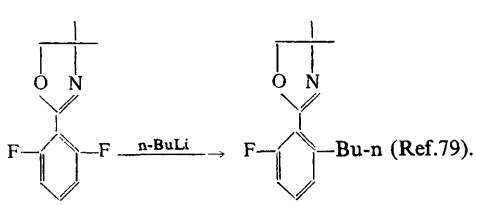


(XVI)

B = MeMgI (yield 16–57%), NaH (17%), KOH (47%), KF (79%).

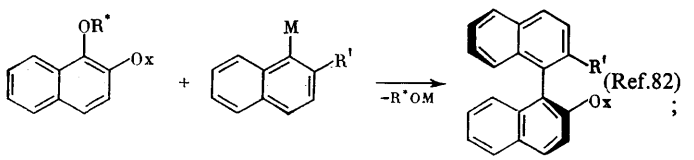
In this case KF proved to be the most effective base.

Several papers have appeared very recently in which the activating influence of the oxazoline group in nucleophilic aromatic substitution reactions has been reported.[78–86] This group is valuable because nucleophilic substitution reactions of various organomagnesium and organolithium compounds occur readily in its presence and the oxazoline group itself may be converted into carboxyl, ester or amide.[78] A fluoride or methoxyl group in the *ortho* position to the oxazoline ring may emerge as leaving group.[78]

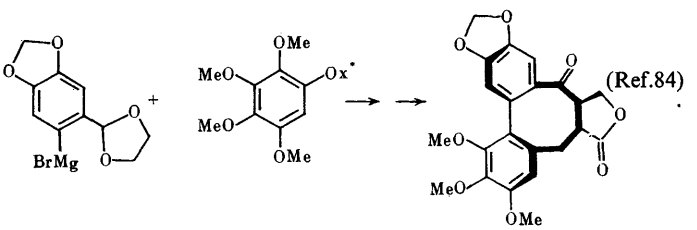


The introduction of the oxazoline group to activate the aromatic nucleus has enabled the development of methods of obtaining chiral biaryls. Good results were obtained both on using a chiral leaving group OR* and a chiral oxazoline fragment OX*.[81–84]
However it is necessary to note that the activating influence of the oxazoline group frequently proved to be insufficient to effect a nucleophilic substitution with stabilised carbanions.

Several studies on the kinetics of the reaction of halonitrobenzenes with carbanions are known.[52,87–96] In all cases the nucleophilic substitution reaction is considered as a two-step process where the rate-determining step is the formation of a 1,1-σ-complex and the removal of halide ion occurs in the subsequent rapid step‡. This is the most common situation for an S_NAr mechanism.[52,87–90]

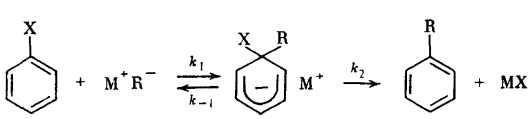


(Ref.82)



(Ref.84)

It should be noted that on the basis of purely kinetic data is is probably impossible in these cases to establish the rate-determining step although indirect data indicate that such a mechanism is correct.[52,87,89] From general considerations it is also evident that the halide removal step (k_2) must not be slower than breakdown of the carbanion (k_{-1}).



This was confirmed by data on the influence of the nature of the leaving group on the rate of halogen replacement in the reactions of *p*-halonitrobenzenes with fluorenyl anions.[91] It was shown that the reaction rate increases in the series F > Cl > Br > I. Results on a study of competing substitution of halogen atom in dihalonitro compounds under the action of anions of malonic and acetoacetic esters are in agreement with this conclusion (see also Table 1).[38–40,43] Similarly for chloropentafluorobenzene reacting with 9-carbomethoxyfluorenyl anion where preferential replacement of the fluoride ion in the *para* position to chlorine was observed.[92,93] Essentially the formation of a 1,1,-σ-complex has not been established in any of the work in which the kinetics of halogen replacement have been studied. It is known that picryl chloride and even 1-halo-2,4-dinitrobenzene form stable 1,3-σ-complexes in reactions with nucleophiles, including carbanions, and these complexes have been isolated and characterised by PMR spectroscopy.[97–99] These complexes are sometimes very stable, as for example in the case of R = CH_2COMe which gave no further substitution product or this conversion occurs very slowly. The 1,3-σ-complexes formed on interacting picryl chloride with anions of malonic and cyanoacetic esters[52,88,89] or malondinitrile[90] are seemingly less stable (lower pK_a values for the CH-acid) and subsequently rearrange into 1,1-σ-complexes (not recorded) which also give substitution products.

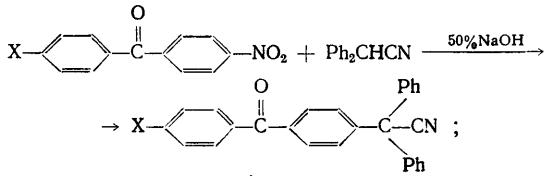
‡The rate-determining removal of halide ion has been proposed.[95,96] However the conclusions were incorrect since these authors proceeded from the false premise of assuming the 1,1-σ-complex to be more stable than the 1,3-σ-complex.

When the group being replaced is MeO^- the second step may remain slow. Such a situation was observed in the reaction of 2,4,6-trinitroanisole with anions of malonic and cyanoacetic esters.[100,101]

It was noted above that high yields of halogen substitution products were successfully achieved on carrying out the reaction in DMSO or under PTC conditions, i.e. in systems where carbanions are in the form of free ions or solvent-separated ion pairs. On the other hand in systems of NaH (or $NaNH_2$)–ether (or THF, benzene) yields of products were, as a rule, low.[54] In these solvents carbanions usually form contact ion pairs or associates. Similar rules for the influence of the medium or of the counter-ion were confirmed by results on the study of the kinetics of arylation of the Na salts of cyanoacetamides and of the K salts of 9-carbomethoxyfluorene by halonitrobenzenes. Here the free ions react at a greater rate than the ion pairs.[92,93,102] The exception was the arylation reaction of the Na salt of *N,N*-dimethylcyanoacetamide by *o*-chloronitrobenzene where the ion pair proved to be more reactive than the free ion. The authors linked this with stabilisation of the σ-anionic complex formed by coordination of the counter ion with oxygen of the nitro group.[102]

b) Replacement of other groups

It is known in principle that the nitro group is a fairly good leaving group under conditions when it is activated by another electron-accepting substituent.[4] Examples of such substitution under the action of carbanions are sparse as yet. The substitution of a nitro group in nitrobenzophenones occurs readily under PTC conditions.[54]

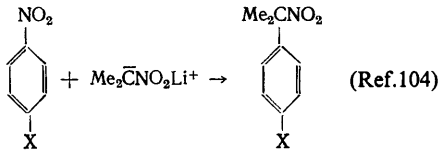


X=H, Cl, Br, F, OMe.

Replacement of a nitro group also takes place in the reaction of perfluoronitrobenzene with perfluoro-t-butyl anion.[103]

$$C_6F_5NO_2 + (CF_3)_3C^- \rightarrow C_6F_5C(CF_3)_3.$$

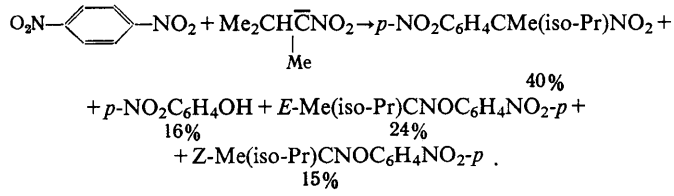
Anions of nitroalkanes (Li salts of 2-nitropropane, 2-nitrobutane[104] and 2-R-5-nitro-1,3-dioxan[105,106]) were used in the majority of studies on nitro group substitutions.



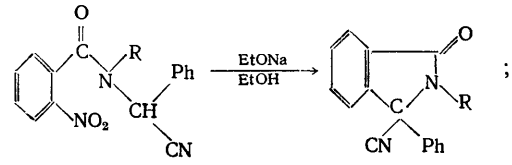
X = NO_2, CN, SO_2Ph, COOMe, COPh.

It was noted that tetrabutylammonium salts of nitroalkanes are more reactive than Li salts.[107,108] For example the reaction of *p*-dinitrobenzene (*p*-DNB) with tetrabutylammonium salts in DMSO, benzene and acetone was complete in less than 5 min while with Li salts only after 3 to 30 h.[107]

The reaction of *p*-DNB with 1,2-dimethyl-1-nitropropane anion in benzene and in DMSO occurs in a more complex manner. In addition to the normal substitution product *p*-nitrophenol and *p*-nitrophenyl ethers of methylisopropylketoxime were formed.[107,108]

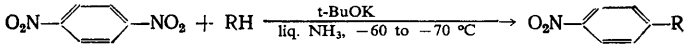


Some intramolecular substitution reactions of an *ortho*-nitro group with ring formation are known.[109]



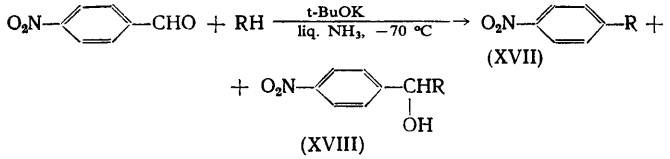
R = Me, $PhCH_2$.

The reacting carbanions may be obtained *in situ* from the corresponding CH-acids in the presence of t-BuOK as was shown for the reaction of *p*-DNB with various RH in liquid NH_3.[110]



R = CH_2COMe, CH(Me)COEt, CH_2COOEt, CH_2CN, CH(Ph)CN etc.

In the case of *p*-nitrobenzaldehyde an unusual substitution was observed under these conditions when fission of a carbon-carbon bond occurred.[111]

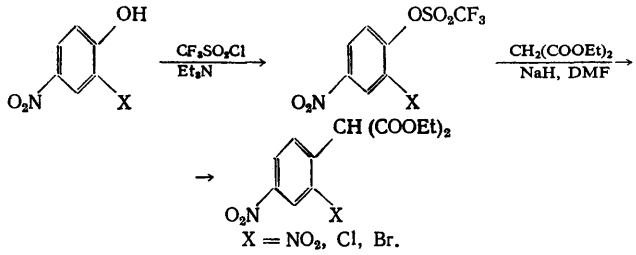


R = CH_2COOMe, CH_2COBu-t, CH_2COOEt, CH(CN)Ph etc.

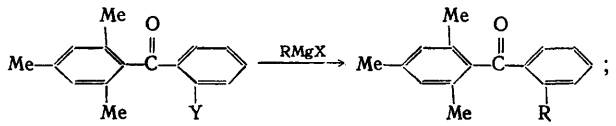
The reaction of *p*-nitrobenzaldehyde with t-BuCOMe was carried out in the presence of various bases. It turned out that systems of t-BuOK/liq.NH_3 and KNH_2/liq.NH_3 were the most effective, yields of substitution products (XVII) were 64% and 71% respectively. The use of other systems, and particularly t-BuOK/t-$BuNH_2$, t-BuOK/THF, t-BuOK/ether, t-BuOK/DMF, $NaNH_2$/liq.NH_3 led to a lower yield of product (XVII). On using the n-BuLi/THF system only alcohol (XVIII), R = CH_2CO-t-Bu was obtained in 76% yield. The reaction mechanism is unknown. Strictly speaking the mechanism has not been established and it is possible, for the nitro group substitution reactions enumerated above, that an $S_{RN}1$ mechanism is effected in some of them.

One of the best leaving groups in reactions of the S_NAr type is the triflate group which is replaced more readily than a nitro group. The example given below illustrates the possibility of applying the

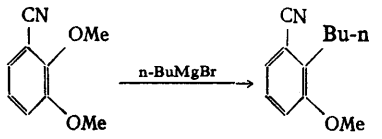
reaction to the synthesis of nitroarylmalonic esters (and nitroarylacetic acids and oxindoles in general) from the corresponding phenols.[112]



There is also information on other groups. For example methylphenylketones, having a leaving group Y in the *ortho* position, react with RMgX with the formation of products of the aromatic substitution of Y.[113–115]



Replacement of the OR group under the action of a Grignard reagent has been shown.[116–118]

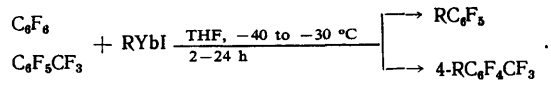


The majority of the carbanions considered in S_NAr reactions are ambident which raises the question of possible arylation at two centres. It is noted that the nature of the leaving group is one of the principal factors controlling the direction of *C*- and *O*-arylation of alkali metal salts of carbonyl compounds. For example the quantity of *C*-isomer falls along the series OPh < Hal < OMe < OAc < OSO_2Me in the reaction of picryl chloride with enolates of β-dicarbonyl compounds with an increase in the hardness of the leaving group. The structure of the enolate, the nature of the alkali metal and the solvent also influence the course of the reaction in a substantial manner. Other conditions being equal the use of softer enolate ions, cations of a lower radius and less polar aprotic solvents aid the preference for *C*-isomer formation.[119–122]

2. Nucleophilic substitution reactions in perfluoroarenes

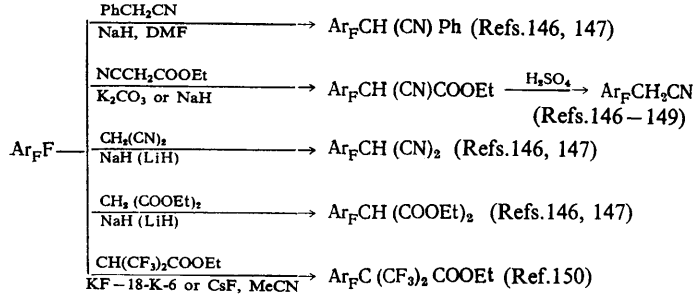
As already mentioned in the Introduction perfluoroarenes react fairly readily by the S_NAr type reaction both with organolithium and with organomagnesium compounds and with carbanions. Aryl (Ph, 3,5-dibromopyridyl, thienyl) and alkyl (Me, Bu) groups have been introduced into the perfluoroaromatic ring by the action of RMgX or RLi.[123–141] Yields of substitution products were fairly high (up to 70%) in several cases, however the reactivity of organomagnesium compounds occasionally proved to be inadequate and the more reactive lithium derivatives led to the formation of disubstitution byproducts. Even in the case of the less reactive propenyl and acetylenyl lithium derivatives a mixture of mono- and disubstituted products was formed as a rule.[138–141]

It was shown comparatively recently that organoytterbium compounds are excellent nucleophilic reagents in substitution reactions at vinyl and aromatic carbon atoms.



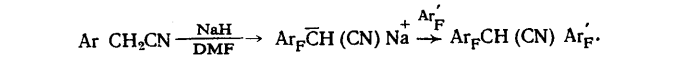
A comparative study of nucleophilic substitution reactions of perfluoroarenes under the action of RYbI, RLi and RMgX (R = Ph, Bu, PhC≡C) showed that RYbI (R = Ph, Bu) surpassed RLi in selectivity of substitution and the more preferred RMgX in the yield of desired products. However of the phenylacetylenyl derivatives only PhC≡CLi was capable of replacing fluoride ion in reactions with C_6F_6 or $C_6F_5CF_3$.[144] It is noted that iodine in pentafluoroiodobenzene is replaced by the action of copper phenylacetylide.[145]

Various carbanions, generated *in situ* from CH-acids using NaH, LiH, K_2CO_3 (usually in DMF), KF or CsF as bases, are involved in nucleophilic substitution reactions with perfluoroaromatic compounds.[146–150]

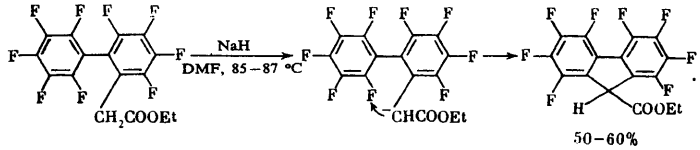


Fairly forcing conditions (100–135 °C) are required to carry out such reactions and then yields of substitution products are moderate (20–60%). However reactions proceeded as a rule at room temperature when using perfluoroarenes with electron-accepting substituents of the type of CN, CF_3 or $C(CF_3)_3$ but yields of products were significantly increased (70–85%).

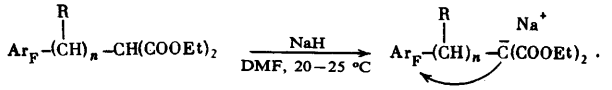
The polyfluoroarene-containing compounds obtained in this way were strong CH-acids. The carbanions corresponding to them, possessing a poorly screened reaction centre, are fairly active reactants in S_NAr type reactions and are used for example for the synthesis of perfluorinated benzhydryl derivatives.[149]



The anion of ethyl polyfluorinated diphenylacetate has been suggested for the synthesis of fluorinated fluorene.[151,152]

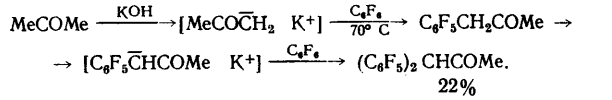


This example may be considered as a particular case of a general method of obtaining polyfluorinated carbocyclic compounds by the intramolecular nucleophilic substitution of a fluorine atom by aralkyl substituted malonic or cyanoacetic esters.[147]



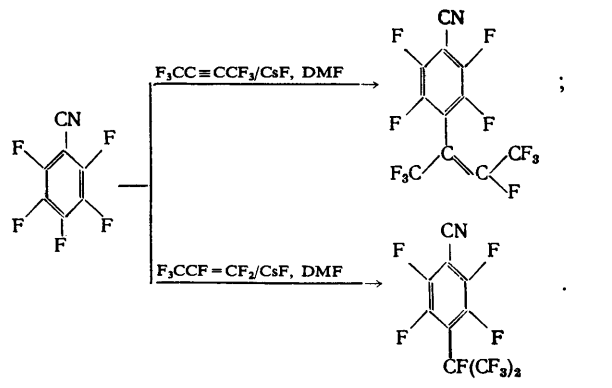
Derivatives of indane (n = 2), acenaphthene (n = 2) and 9,10-dihydrophenanthrene (n = 1, Ar = $C_6H_5C_6F_4$-2) were obtained in this way.[153,154]

Ambident anions may react with perfluoroarenes at both reaction centres. Thus anions of acetoacetic ester[155,156] and acetophenone[157] react with hexafluorobenzene and perfluorotoluene at a carbon atom with subsequent intramolecular cyclisation at oxygen with the formation of 4,5,6,7-tetrafluorobenzofurans (80–140 °C). At lower temperatures the reaction was successfully stopped at the *C*-arylation stage.[157,158]

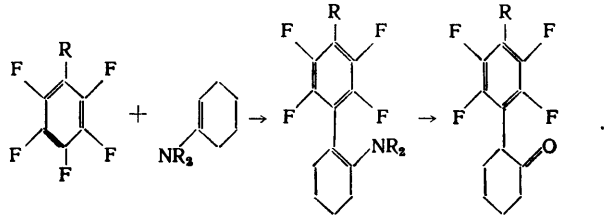


However depending on the nature of the substrate, solvent and enolate ion a mixture of *O*- and *C*-isomers or even predominantly the *O*-isomer may be formed. Thus replacement of fluoride ion by acetate or mesylate in octafluorotoluene leads preferentially to *O*-arylation of the potassium derivative of acetoacetic ester (DME, dimethylacetamide, EtOH).[122] On interacting the anion of pentafluoroacetophenone with $C_6F_5CF_3$ a mixture of *O*- and *C*-arylation products is formed the ratio of which depends on the nature of the solvent.[158]

The reaction of perfluoroaromatic compounds with perfluoroalkenes or alkynes in the presence of fluoride ion is of particular interest since it is a nucleophilic variant of the Friedel–Craft reaction.[103,159,160]



It is possible to obtain ketones, esters and amides containing a perfluoroaryl group in the α position by condensation of α,β-unsaturated amines with perfluoroarenes.[161]

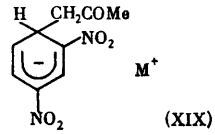


III. Preparation of anionic σ-complexes with C–C bonds

One further route to introduce a C–C bond into electron-deficient arenes comprises the preparation and oxidation of anionic σ-complexes, including 1,3-σ-complexes, containing good leaving groups of the halogen type in the aromatic ring.

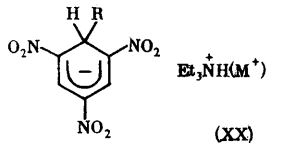
1. Reaction of aromatic compounds with carbanions and heteroorganic compounds

The simplest method of obtaining anionic σ-complexes of aromatic compounds containing electron-accepting groups (NO_2, CN, SO_2CF_3, etc.) with carbanions is the interaction of an aromatic substrate with a CH-acid in the presence of base. The possibility of forming stable complexes of such type was shown for the first time by Janovsky[162,163] in 1886 in the reaction of *m*-dinitrobenzene (*m*-DNB) with alkaline aqueous acetone. However only in 1963 was this σ-complex successfully isolated in the solid state[164] and its structure demonstrated.[165]



(XIX)

Historically most work is linked with the study of σ-complexes of nitroaromatic compounds with the acetonyl anion. Potassium carbonate,[166] alkali metal hydroxides and alkoxides[164,167–169] and amines[170,171] were used as bases for their preparation. The σ-complex of 1,3,5-trinitrobenzene (TNB) with acetonyl anion was obtained on carrying out the reaction in an acetone medium (~20–30 fold excess) in the presence of a twofold excess of KOH (spectro-photometric check). The yield of (XX) for R = CH_2COMe was 73%.[164]



(XX)

It was shown by PMR spectroscopy that in the presence of triethyl- or diethylamine TNB forms a σ-complex (XX) with various ketones which simultaneously serve as solvents [R = CH_2COMe, CH(Me)COEt, CH(Ph)$COCH_2Ph$, $CH(CH_2)_4CO$, $CH(CH_2)_3CO$,[170,171] $CH(CH_2)_5CO$, CH_2COPh], yield was 78%.[172]

These complexes may readily be isolated by precipitation with ether. With unsymmetrical ketones such as methylethylketone a mixture is formed of the isomeric complexes (XX) [R = CH_2COEt or CH(Me)COMe].[171] The exception was methylisopropylketone, in this case only one complex is formed of type (XX) (R = CH_2COPr-iso).[170]

To obtain complexes of TNB with anions of *para* substituted acetophenones XC_6H_4COMe (X = NO_2, OMe, CN) the reaction was carried out in dioxan in the presence of a large (~20 fold) excess of Et_3N.[172] In this case a twofold quantity of the CH-acid

was used (yields of complexes were not indicated). Complexes of TNB with anions of α-haloketones were obtained on carrying out the reaction in MeCN in the presence of Et_3N.[173]

The formation of adducts (XX) with anions of nitroaliphatic compounds [R = CH_2NO_2, $CH(Me)NO_2$, $CH(Et)NO_2$, $C(Me)_2NO_2$],[174] acetonitrile,[175] propionaldehyde[176] and phenylacetonitrile[170] was demonstrated by PMR spectroscopy. In all cases the reaction was carried out in the presence of a large excess of CH acid. The complex of TNB with nitromethane anion was isolated using NaH as base (yield was 35%).[177] An equimolar amount of CH-acid was applied to obtain the complex of TNB with the anion of acetylcyclopentadienylmanganese tricarbonyl which is formed in the presence of NEt_3 in a medium of MeCN (50% yield).[178]

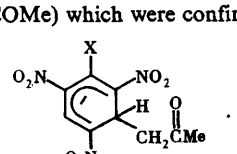
The alkali metal methoxides are effective bases for obtaining anionic σ-complexes.[168,169] Complexes of TNB with anions of acetone, cyclobutanone, cyclopentanone and cyclohexanone were isolated in quantitative yield on carrying out the reaction in a medium of the ketone.[169] To obtain complexes of TNB with cyanoacetic and malonic esters the same authors used an equimolar and double amount of the corresponding CH-acid, reaction was carried out in MeOH and yields of complexes were quantitative.[179] The σ-complexes of TNB with CCl_3 and CBr_3 anions were isolated in yields of 80 and 63%.[180] Reaction in these cases was carried out in DMSO with an excess (10 fold) of chloroform or bromoform in the presence of MeONa. The complex of TNB with the trichloromethyl anion was also formed from trichloroacetic acid and TNB in DMSO. The corresponding substitution product was isolated on oxidation of this complex with bromine in pyridine.[181]

It is known that acetoacetic ester reacts with TNB in the presence of various bases (KOH, Et_3N, MeONa) with the formation of a bicyclic complex (see Chapter III, section 3). However on interacting TNB with potassium-acetoacetic ester a complex of type (XX) [R = CH(COMe)COOEt] was also obtained in 33% yield.[182]

Finally σ-complexes of TNB with the anions of DMF, dimethylacetamide and DMSO were synthesised in the presence of KOH or Bu_4NOH in a dioxan medium. In each case the CH-acid was introduced in excess (yields of complexes were 40, 75 and 80% respectively).[183] The σ-complex of TNB with indole was obtained in 60–90% yield in the two-phase system $CH_2Cl_2-H_2O-NaOH$ in the presence of *N*-methylquinolinium, *N*-methylisoquinolinium or tetramethylammonium salts.[184]

As already mentioned a methyl group located in the *para* position to a nitro group in polynitro aromatic compounds may be deprotonated by the action of base in polar solvents (DMSO). The resulting carbanion reacts with TNB giving anionic σ-complexes.[185,186] On using equimolar amounts of CH-acid and KOH or MeONa as base complexes of TNB were isolated (yield ~50%) and characterised with anions of 2,4,6-trinitrotoluene,[185,186] 2,4-dinitrotoluene, 4,6-dinitro-*m*-xylene and 2,4,6-trinitro-*m*-xylene.[186] Addition of two molecules of TNB is possible (in an excess of base) for the latter.

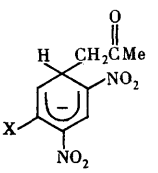
In the presence of Et_3N, MeONa or KOH 1-X-2,4,6-trinitrobenzene (X = OEt, OMe, OPh, Me, Cl, NMe_2, COOH, COOMe, SMe) reacts with acetone forming 1,3-σ-complexes (XXI) (R = CH_2COMe) which were confirmed by PMR spectroscopy.[98,187–189]



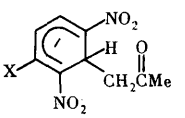
(XXI)

In contrast to ketones which form stable 1,3-σ-complexes with 1-X-2,4,6-trinitrobenzene, the stronger CH-acids such as acetoacetic, malonic, and cyanoacetic esters, and malondinitrile react with 1-X-2,4,6-trinitrobenzene (X = OMe, OCOMe, Cl, OAr) in the presence of MeONa giving 1,3-σ-complexes which rearrange into 1,1-σ-complexes with the subsequent formation of a substitution product.[52,88–90,100,101]

It is known that anionic complexes of *m*-dinitrobenzene (DNB) derivatives are far less stable than complexes of TNB. For example, the equilibrium constant of the complex of TNB with methoxide ion is 17 $lit.mol^{-1}$ and for the complex of *m*-DNB with methoxide ion the equilibrium constant is only 1×10^{-6} $lit.mol^{-1}$.[190] As mentioned above the σ-complex of TNB with acetonyl ion was obtained in 73% yield on using KOH as base. Under the same conditions *m*-DNB gave a σ-complex in only 34% yield.[164] Similarly 1-X-2,4-dinitrobenzenes react in alkaline medium with acetone with the formation of the isomeric complexes (XXII) and (XXIII).



(XXII)

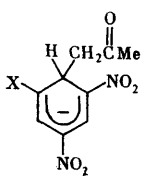


(XXIII)

A σ-complex (XXII) is mainly formed when X = H, OMe, COOMe, Cl, Br, I, Me, n-Pr, n-Bu, or SO_2Ph[99,164,191–193] but when X = F, SEt, SCN, or SPh a σ-complex of type (XXIII) predominates.[164,192,193] On carrying out the reaction in an acetone medium and using KOH as base the yield of complexes was 10–35% overall.[99,164,191–193,195] However on using alkali metal (Na, K, Rb, Cs) methoxides the yields of σ-complexes became almost quantitative.[167]

The σ-complexes of 2,4-dinitronaphthalene, 2,4,5,7-tetranitronaphthalene and 9-nitroanthracene with acetonyl and nitromethyl anions have been obtained and characterised.[174,187]

1-X-3,5-Dinitrobenzenes react in alkaline medium with acetone giving two isomeric products (XXIV) and (XXV). When X = OMe or Me only complexes (XXIV) were obtained in 7.5 and 18% yield in the presence of KOH.[194] A mixture of σ-complexes (XXIV) and (XXV) was formed when X = COOEt,[194,195] CF_3,[194–196] CN,[196] COOMe and COO^-,[197] $CONH_2$ and $CONMe_2$.[198]



(XXIV)



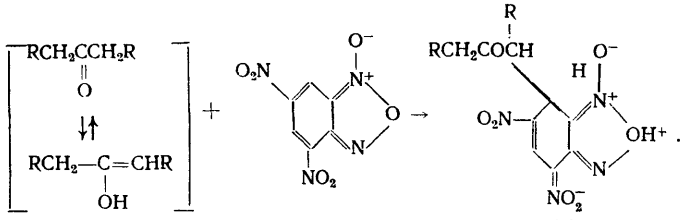
(XXV)

Isomerisation constants were measured for σ-complex (XXIV) going to (XXV), which had been obtained from the enolates of cyclohexanone and 1-X-3,5-dinitrobenzene [X = $CON(CH_2)_5$, COOMe, CN].[199]

Complexes obtained from 1,3,5-*tris*-(trifluoromethylsulphonyl)-benzene (TFMSB) proved to be several orders of magnitude more stable than complexes of TNB. The complex of TFMSB with

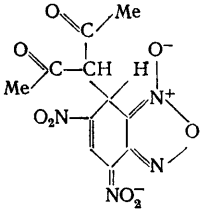
acetonyl anion using KOH in acetone as base was isolated in 24% yield[200] but on using EtOH the yield was 97%.[177] The complex of TFMSB with nitromethane anion was isolated (67% yield) using NaH.[177] Complexes of TFMSB with the anions of diethyl malonate and propionaldehyde were not isolated but were oxidised to the corresponding substitution products.[201]

4,6-Dinitrobenzofuroxan (DNBFX) and 4,6-dinitrobenzofurazan (DNBFZ) are even stronger electron-accepting substrates capable of forming anionic σ-complexes even in the absence of base. DNBFX reacts with water and methanol in the absence of base forming hydroxyl and methoxyl complexes and also with ketones. The formation of σ-complexes (XXVI) with anions of acetone, cyclopentanone, cycloheptanone, pentane-2,4-dione and 3-methylpentane-2,4-dione has been demonstrated.[202] It was proposed that reaction was effected with the enolic form of the ketone or with the enolate ion formed as a result of its partial ionisation.[202]

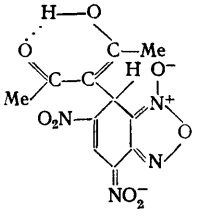


(XXVI)

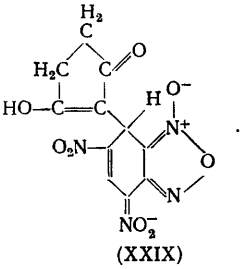
β-Dicarbonyl compounds like pentane-2,4-dione or cyclopentane-1,3-dione give adducts which may exist both in the ketonic (XXVII) and in the enolic forms (XXVIII) and (XXIX).[202]



(XXVII)



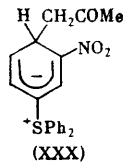
(XXVIII)



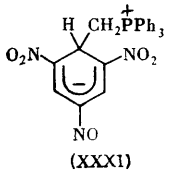
(XXIX)

Compounds DNBFX and DNBFZ form complexes even with such weak bases as 1,3,5-trimethoxybenzene (see also p. 765).[203]

Zwitterionic σ-complexes (XXX) and (XXXI) were obtained by the reaction of an alcoholic solution of KOH with an acetone solution of *m*-nitrophenyldiphenylsulphonium fluoroborate[204] and methylenetriphenylphosphorane with TNB.[205]



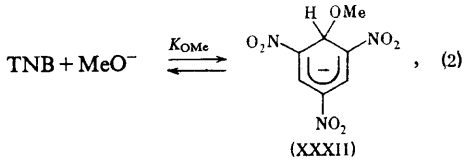
(XXX)



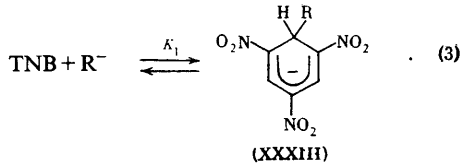
(XXXI)

The kinetics of formation and stability constants of σ-complexes of TNB with appropriate carbanions have been studied for a series of CH-acids in the presence of MeONa.[179,90] The following scheme has been proposed for the formation of a σ-complex with a C–C bond where the limiting step is the addition reaction of carbanion to TNB [reaction (3)].

$$RH + MeO^- \overset{K}{\rightleftarrows} R^- + MeOH, \quad (1)$$



(XXXII)



(XXXIII)

Rate constants are given in Table 2 for the formation and dissociation (k_1 and k_{-1}) of σ-complexes of TNB and also the equilibrium constant (K_1). It is seen from the data given in Table 2 that the stability of σ-complexes falls as the strength of the CH-acid increases. It was reported[179] that TNB complexes with a C–C bond possess a higher stability than complexes with *O*-nucleophiles. The complex with acetone is more than 10 orders of magnitude more stable than the complex with methoxide. The anions of methyl acetate, methyl cyanoacetate, dimethyl malonate and malondinitrile are less basic than MeO^- but their complexes with TNB proved to be more stable than methoxyl [the equilibrium constant for the formation of complex (XXXII) K_{OMe} = 17 lit.mol^{-1} is comparable only with the equilibrium constant for the formation of the least stable complex of TNB with methyl acetoacetate]. The high stability of complexes with enolate ions is confirmed also by the low values for the decomposition rate constants of σ-complexes (in certain cases values of k_{-1} are so low as to be difficult to measure).[172]

Table 2. Kinetic and equilibrium parameters for the reaction of TNB with carbanions in methanol.[179]

Carbonyl compounds	K, lit. mol^{-1}	k_1, lit. mol^{-1}.sec	k_{-1}, sec^{-1}	K_1, lit.mol^{-1}
MeCOMe	10^{-6}	$3.30\cdot10^{6}$	$8.2\cdot10^{-6}$	$4\cdot10^{11}$
	10^{-4}	$1.62\cdot10^{5}$	$1.76\cdot10^{-4}$	$9.2\cdot10^{8}$
$CH_2(COOMe)_2$	0.5	$2.5\cdot10^{5}$	20.5	$1.22\cdot10^{4}$
$CH_2(CN)COOMe$	54	$1.3\cdot10^{5}$	62	$1.66\cdot10^{3}$
$CH_2(CN)_2$*	590	$3\cdot10^{5}$	$6.5\cdot10^{3}$	40
$MeCOCH_2COOMe$	418	$5.5\cdot10^{3}$	470	11.7

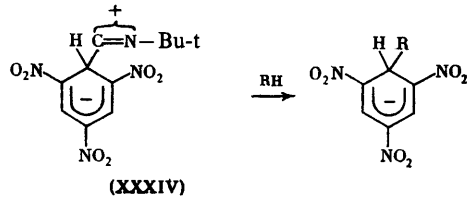
*Literature data.[90]

In the majority of the reactions described above the CH-acid which is a source of carbanion is taken in excess and frequently serves as solvent. The excess of CH-acid may be avoided if the

reaction is carried out in a two-phase system of solid base–solvent. At the same time the use of such a system makes it possible to extend significantly the limits of the pK_a of the CH-acids entering into the reaction. Thus in the system THF–solid base (KF, K_2CO_3, KOH)–18-crown-6 ether the σ-complexes of TNB with such radicals R as CH(Ph)COOEt(Me), CH(Ph)CN, C_6F_5 or fluorenyl were successfully obtained.[206] These complexes contain 1 mole 18-crown-6 ether in their composition. The complexes had been obtained previously by reactions with organomercury and organotin compounds.[207–210] The weakest CH-acid which reacts with TNB under these conditions (KOH as base, KF and K_2CO_3 proved to be ineffective) was pentafluorobenzene. Phenylacetylene (pK_a 29.4 in DMSO[211]) did not react with TNB even in the presence of KOH. It should be mentioned that the final result of the reaction depends not only on the base strength and on the CH-acid but also on the stability of the σ-complex (XXXII) of aromatic substrate with base, the formation of which often precedes the formation of a σ-complex (XXXIII) with the carbanion. For this reason KF proved to be a more effective base than K_2CO_3. The stability of the σ-complex formed with base may explain the fact that TFMSB, which significantly surpasses TNB in electrophilicity, reacts under PTC conditions only with fairly strong CH-acids, such as diethyl malonate, when, as for TNB, a σ-complex was obtained with anions of weaker acids such as phenylacetonitrile, ethyl phenylacetate, pentafluorobenzene or fluorene.[206]

Not only CH-acids but also organometallic compounds have been used to obtain σ-complexes. It was shown by PMR spectroscopy that organomercury compounds R_2Hg (or RHgX), where R = CH_2COMe, CH(Ph)COOEt, CCl_3, C_6F_5, $CH(CF_3)_2$ or *o*-carboranyl, react with TNB forming σ-complexes (XX) under conditions of nucleophilic catalysis with iodide ion.[207,208] Some organotin compounds $RSnMe_3$, where R is acetonyl, fluorenyl, indenyl or cyclopentadienyl also successfully react with TNB. In this case the solvent DMSO played the role of nucleophilic catalyst.[209,210]

It has been shown possible to use organocopper and organotin compounds for the synthesis of σ-complexes with TNB. Reactions of TNB with phenyl- and 2,6-dimethoxyphenylcopper,[212] 2,6-dimethoxy- and 2,4,6-trimethoxyphenylsilver,[213] copper and silver phenylacetylides,[214] hexenylcopper,[214] 2-furyl- and 2-thienylcopper,[215] acetylcyclopentadienylmanganese tricarbonylsilver,[216] cyclopentadienyl- and indenylsilver[217,218] occur at room or lower temperatures in pyridine or quinoline. Organocopper compounds proved to be somewhat more reactive than silver derivatives. The σ-complexes were isolated in some cases[212,213,215–218] and were oxidised to the corresponding substitution products (see chapter III, section 5). The interesting σ-complex (XXXIV) was obtained from TNB and t-BuNC in the presence of copper or Cu_2O.[219] Complex (XXXIV) was unstable and reacted with CH-acids with the formation of σ-complexes with CCl_3, indenyl, and cyclopentadienyl anions.



(XXXIV)

Organosilicon compounds $RSiMe_3$ also react with TNB with fluoride ion catalysis. These were of various types, benzyl and allyl derivatives, silylated ketones, ethers and acylsilanes (pK_a of the corresponding RH was 20–35) and form ionic σ-complexes in good and occasionally quantitative yield.[220,221]

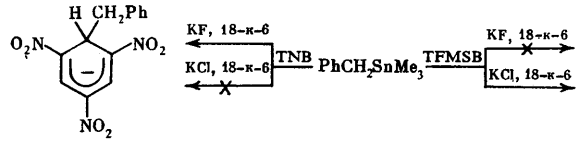
$$TNB + RSiMe_3 \xrightarrow[THF]{KF,\ 18\text{-}K\text{-}6} [TNB.R']K^+.(18\text{-}K\text{-}6),$$

$$R = \bigcirc\!\!-O-,\quad R' = \bigcirc\!\!=O,$$

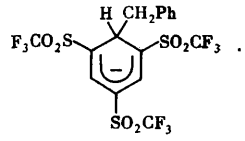
R = R′=CH_2COOMe, CH_2COOEt, CH_2COEt, COPh, COMe, CH_2Ph, All, C≡CPh.

It should be mentioned that organosilicon reagents have proved to be useful in the synthesis of various σ-complexes which are difficult to obtain by other routes, such as σ-complexes with alkyl (CH_2Ph, $CH_2CH=CH_2$) and acyl (COMe, COPh) groups. The application of organosilicon compounds has enabled the selective introduction of the trinitrophenyl group into unsymmetrical ketones while the reaction of TNB with these ketones in the presence of base gives a mixture of isomers. In certain cases, for example when obtaining complexes $[TNB.C{\equiv}CR]^-$ and $[TNB.\overline{CH-(CH_2)_4-CO}]^-$, the use of $RSiMe_3$ is more convenient than CH-acids or organo-silver or copper compounds and gives better yields.

TFMSB, in contrast to TNB, reacts under conditions of catalysis by fluoride ion only with the most reactive of the $RSiMe_3$ studied, viz. the trimethylsilyl ether of cyclohexanone enol. In all the remaining cases the reaction stops at the stage of forming an anionic σ-complex with fluoride ion. It was mentioned above that the same result was observed in reactions of TFMSB with CH-acids. In the presence of fluoride ion TFMSB does not form a σ-complex with a C–C bond even with $PhCH_2SnMe_3$, while TNB reacts readily, giving complex (XXXV). However to obtain the σ-complex of TFMSB with a $PhCH_2$ group (XXXVI) it was sufficient to replace fluoride ion by chloride ion which also forms a complex with TFMSB but is undoubtedly less stable than the complex with fluoride. It has been reported that complex (XXXV) was not formed in the reaction of TNB with $PhCH_2SnMe_3$ in the presence of KCl.[211]



(XXXV)

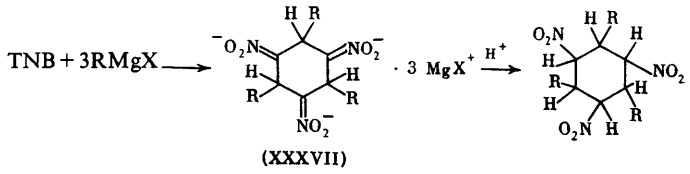


(XXXVI)

Organosilicon compounds have also been proposed for introducing C–C bonds into 1-X-2,4-dinitrobenzenes. However the complexes formed were less stable than complexes of TNB and their oxidation was carried out without isolation (see p. 763–764).[222]

Organolithium and organomagnesium compounds are used as a carbanion source for CH-acids with pK_a 30–33. However TNB adds three molecules of RMgX on carrying out the reaction in ether

or THF giving 1,3,5-trialkyl-2,4,6-trinitrocyclohexanes [the intermediate (XXXVII) was not identified] on acidification of the reaction mixture.[223,224]



(XXXVII)

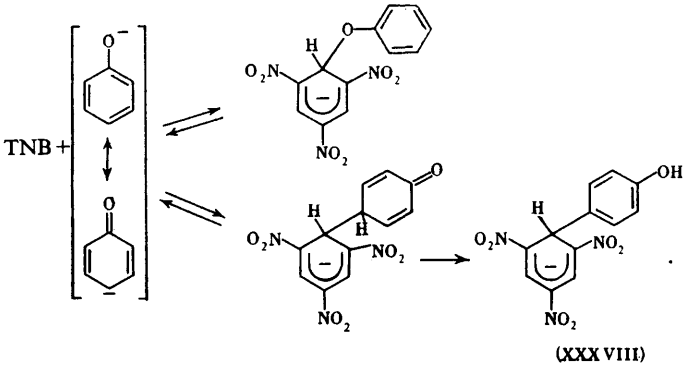
R = Me, Et, n-Pr, n-Bu, iso-Bu.

The reaction of RMgX with *m*-DNB, 1-chloro-2,4-dinitrobenzene and 2,4-dinitroanisole proceeds in a similar manner.[225] However in the majority of cases the reaction of organolithium and organomagnesium compounds with polynitroaromatic compounds gives a mixture of products of oxidation-reduction reactions and addition reactions at the nitro group. Consequently it is a fairly complex problem to obtain anionic σ-complexes from weak CH-acids (pK_a > 30–33). Taylor has succeeded in obtaining σ-complexes of TNB with methyl and n-butyl groups using the appropriate tetraalkylboron salts $Alk_4B^-Me_4N^+$ (or Ph_4As^+).[226]

σ-Complexes with Me_3ECH_2-groups, where E = Si, Sn or Ge, were obtained in a similar manner.[227] On using tetraalkylammonium salts $(CH_2EMe_3)_4B^-Me_4N^+$ σ-complexes of TNB with Me_3ECH_2-groups were successfully obtained while the use of lithium salts, such as Me_3SiCH_2Li or $(Me_3SiCH_2)_4BLi$, led to a mixture of unidentified products.[227]

2. Reaction with phenoxide ions and nitrogen bases

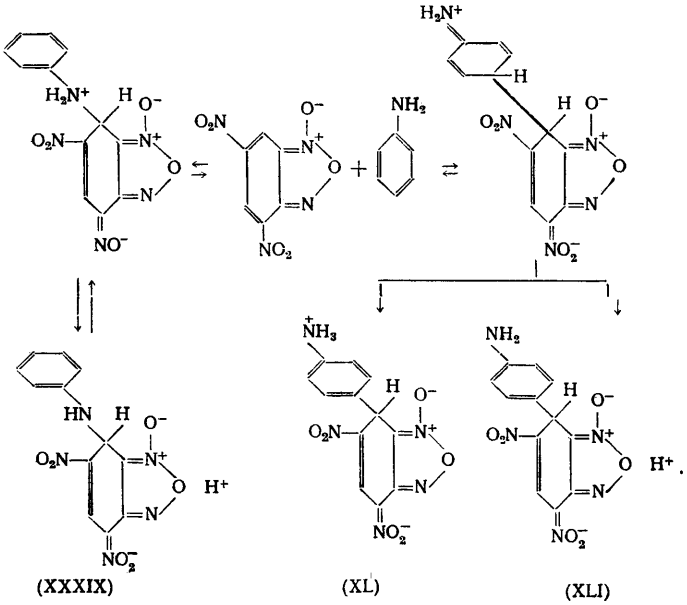
The ability of phenols and aromatic amines to act as *C*-nucleophiles in reactions of the S_NAr type in the presence of base was recorded in Chapter II. Phenoxide ions, anions of nitrogen heterocycles and anilines, in the presence of NEt_3 or 1,4-diazabicyclooctane, also form σ-complexes with C–C bonds in several cases,[228–234] and therefore may be used to introduce homo- or heterocyclic radicals containing strongly electron-donating substituents into electron-deficient aromatic substrates. In the reactions of phenols σ-complexes with C–O bonds are usually the reaction products under kinetic control and then rearrange into complexes with C–C bonds, the reaction products under thermodynamic control.[234]



(XXXVIII)

Adduct (XXXVIII) was obtained by the reaction of TNB with PhOH in DMSO or in DMSO–MeOH in the presence of MeONa (80% yield).[231] A small quantity of the corresponding *ortho* isomer was formed in addition to the *para* isomer (XXXVIII) and was detected by PMR spectroscopy.[231] A bond was formed in the *ortho* position in the complex of TNB with the anion of α-naphthol.[232]

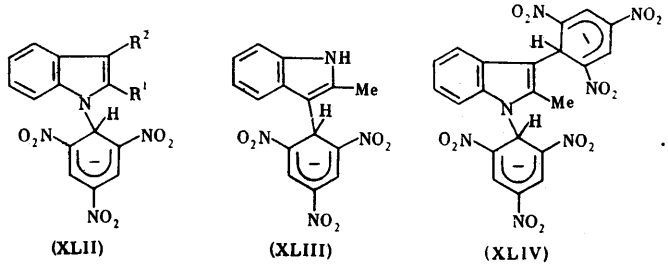
In contrast to phenoxide ion, aniline gives only a complex with a C–N bond with TNB in the presence of Et_3N or 1,4-diazabicyclooctane.[235,236] However with a more strongly electron-deficient substrate like DNBFX, depending on the experimental conditions, it is possible to obtain both a complex with a C–N bond (XXXIX) and a σ-complex with a C–C bond (XL) or (XLI).[237–240] Only complex (XLI) is formed when using equimolar amounts of aniline and DNBFX. The application of a two fold excess of $PhNH_2$ leads to a mixture of products (XXXIX) and (XLI) but on adding Et_3N only complex (XXXIX) was isolated and was established by PMR spectroscopy.[238]



(XXXIX) (XL) (XLI)

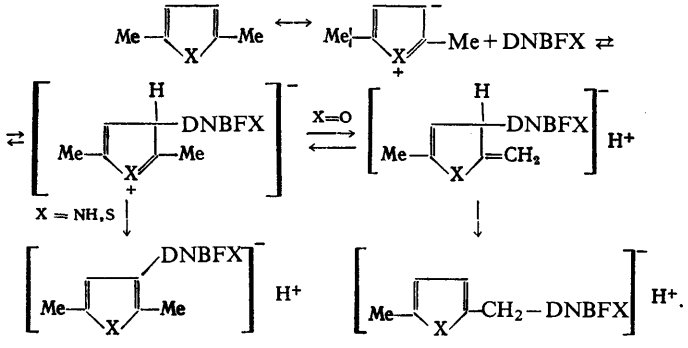
1,8-*bis*-(Dimethylamino)naphthalene reacts with DNBFX or 4,6-DNBFZ giving an adduct of the type of (XLI) in quantitative yield.[241,242]

TNB reacts with nitrogen heterocycles in the presence of base forming a mixture of complexes with C–N and C–C bonds the stability of which is determined by the nature of the heterocycle.[231–234,243–246] Thus 3-methyl- and 2,3-dimethylindoles in DMSO in the presence of MeONa give only complexes with a C–N bond (XLII), while with TNB 2-methylindole forms a mixture of complexes (XLII)–(XLIV) with a predominance of complex (XLIII) which, after some time, becomes the sole product.[243]



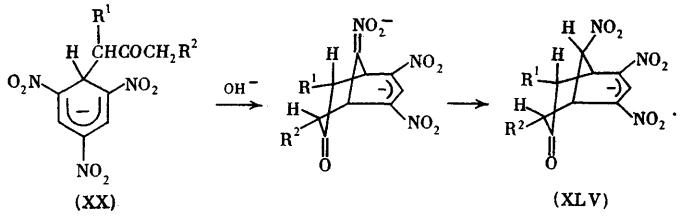
(XLII) (XLIII) (XLIV)

Compounds DNBFX and DNBFZ are also capable of reacting with nitrogen heterocycles in the absence of base.[247–249] Only complexes with C–N bonds are formed with imidazole or with *N*-alkylimidazole and only complexes with C–C bonds are formed with pyrrole, indole, thiophen and their *N*-alkyl substituted derivatives. However a methyl group proved to be more reactive in 2,5-dimethylfuran.[249]



3. Formation of bi- and tricyclic complexes

As mentioned above, the σ-complexes of TNB with anions of ketones are fairly stable. However, in the presence of strong bases such as KOH or NaOH they may be subject to further conversion generally forming bicyclic adducts (XLV).[250]



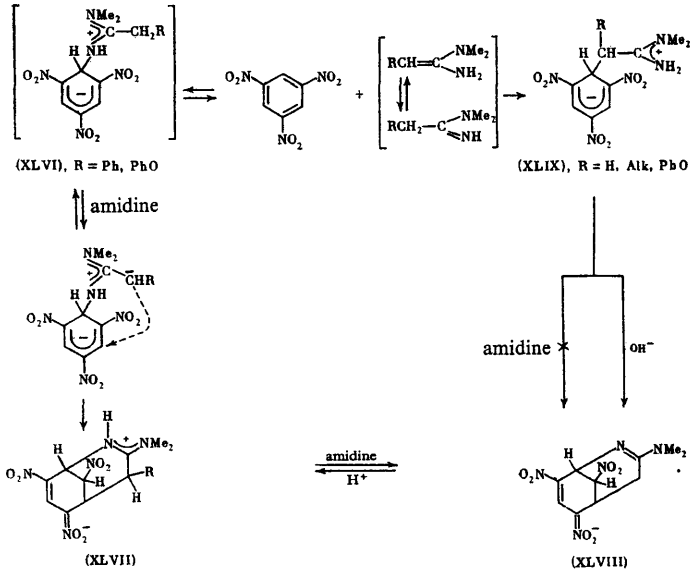
(XX) (XLV)

The reaction stopped at the stage of forming σ-complex (XX) o using Et_3N as base.[170,171] It is interesting that bicyclic adducts wer formed on interacting TNB with ketones in the presence c diethylamine (Et_2NH) although the basicities of Et_3N and Et_2NH are close.[251] It was considered that the corresponding enamines added to TNB in this case.[252] A tricyclic complex was obtained from cyclohexanone in the presence of Et_2NH while cyclopentanone gave the usual σ-complex (XX) with R = $\overline{CH-(CH_2)_3-CO}$.[253]

The only result of interacting TNB with β-dicarbonyl compounds in the presence of Et_3N were bicyclic adducts of the (XLV) type. Complexes of type (XX) were not isolated.[15,254–258] 1-Cyano-3,5-dinitrobenzene, methyl 3,5-dinitrobenzoate, methyl 2,4,6-trinitrobenzoate, picryl amide and picric acid react with β-dicarbonyl compounds (acetoacetic ester, 1,3-dicarbomethoxyacetone) in a similar manner.[254,255,259] Bicyclic products were also formed on interacting 1,3-dicarbomethoxyacetone with dinitro- and tetranitronaphthalenes.[255]

Recently the reaction of nitro aromatic compounds with amidines has been studied intensively.[260–264] The products of these reactions may be of considerable interest to pharmacologists.[260] Generally it is possible to form several complexes (XLVI)–(XLIX) by reacting TNB with amidine (Scheme 1).

Scheme 1



(XLVI), R = Ph, PhO (XLIX), R = H, Alk, PhO

(XLVII) (XLVIII)

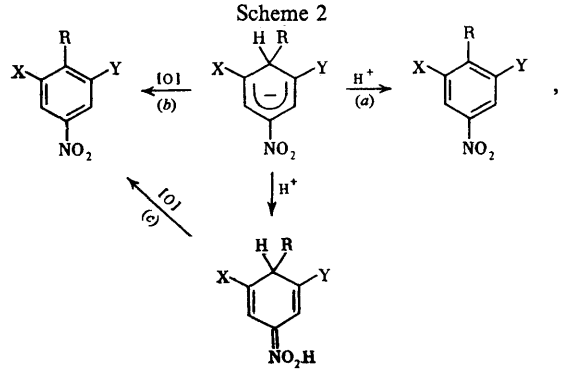
Although the formation of adduct (XLVI) was not confirmed by PMR spectroscopy it was proposed that this particular σ-complex was a precursor in the formation of bicyclic adduct (XLVIII). This conclusion was drawn on the basis that the alternative σ-complex (XLIX), which may occasionally be isolated together with bicyclic product (XLVII), is not converted into (XLVIII) by the action of amidine.[260,262] Complex (XLIX) may be converted into a bicyclic adduct, however it was necessary to apply a stronger base, such as KOH, to carry out the conversion.[261]

Adducts analogous to (XLVIII) were also formed from 1,3-dinitro- and 1,3,6,8-tetranitronaphthalene.[262] With a less strongly electron-deficient substrate, viz. 1-cyano-3,5-dinitrobenzene, no bicyclic adduct was formed.[263] It should be mentioned that products of intramolecular attack by the oxygen atom with the formation of bicyclic adducts were not detected.[253]

4. Oxidation of anionic σ-complexes

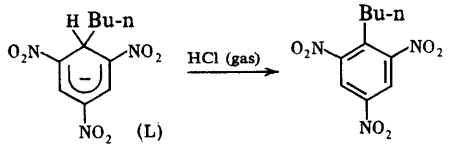
Products of substitution of hydride ion may be obtained from anionic σ-complexes by one of the methods given in Scheme 2:

Scheme 2



(a) action of acid on the σ-complex, (b) oxidation of the σ-complex, (c) protonation of the σ-complex to a nitronic acid with its subsequent oxidation.

It was shown by PMR spectroscopy that 1-n-butyl-2,4,6-trinitrobenzene was formed quantitatively on passing gaseous HCl into a solution of σ-complex (L) in CD_3CN.[226]

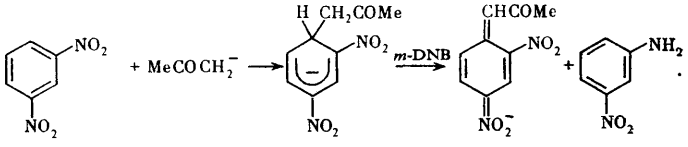


2,4-Dinitrophenylacetone (24%) was isolated on acidifying the Janovsky σ-complex (XIX)§.[265]

On acidification of solutions of anionic σ-complexes there usually occurs either decomposition into starting materials or the formation of nitronic acids which may then be converted into substitution products by the action of a suitable oxidising agent [route (c)]. Substitution products from σ-complexes of TNB with indenyl, cyclopentadienyl,[217,218] 1,3-dimethoxyphenyl,[213] thienyl and furyl[215] groups have been obtained in the same way.

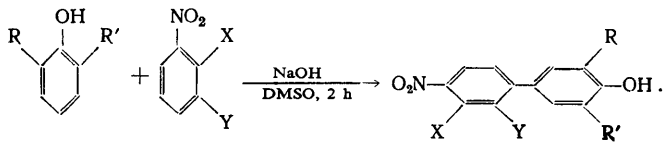
Most frequently σ-complexes are oxidised directly [route (b)]. It has been shown[218] that product yields on oxidation of σ-complexes of TNB (R is indenyl, cyclopentadienyl) with 1,4-benzoquinone or H_2O_2 were somewhat lower than on using method (c) [2,4,6-trinitrophenylcyclopentadiene was obtained in 80% yield by method (c) and in 52% yield by method (b)].

Occasionally the role of oxidising agent may be fulfilled by the initial nitroaromatic compound. Such a situation is brought about in, for instance, the known Zimmerman reaction.



The presence of *m*-nitroaniline among the reaction products supports this scheme.[266,267] A similar case has been described.[63]

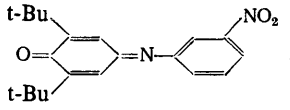
The reaction of *m*-DNB and of *m*- and *o*-cyanonitrobenzenes with 1,6-dialkylphenols (Alk = t-Bu or Me) in alkaline medium leads to a diaryl (28–69% yield). In the case of an unsubstituted phenol the yield of products fell to 17%. Mononitro compounds (nitrobenzene, 2-nitroacetophenone, 9-nitroanthracene) react differently with phenols but TNB forms only a σ-complex.[63]



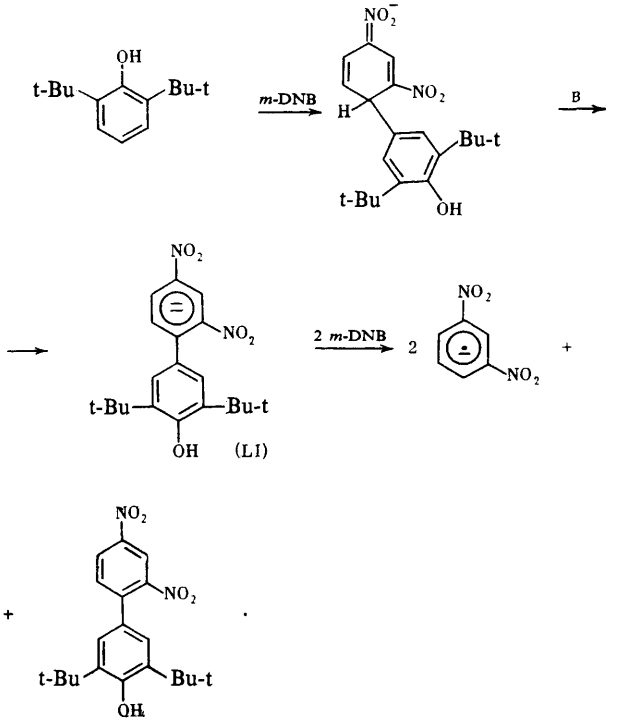
R, R′=Alk; X=H: Y=NO_2, CN; X=CN: Y=H.

§The formation of substitution products has also been recorded in other cases. However their yields did not exceed 10–15%.[188,214]

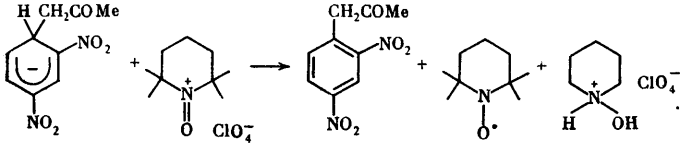
It is possible that the reaction mechanism comprises formation of a σ-complex and subsequent oxidation of it by nitroarene to the diaryl.[63,268] The imine



was detected among the products of reaction with *m*-DNB, i.e. reduction of the nitro compound occurred during the course of the reaction.[63]

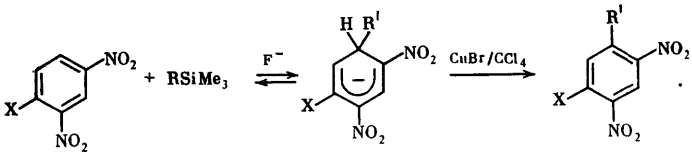


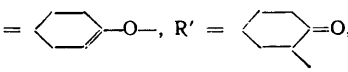
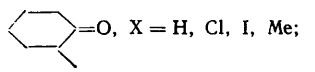
The oxidation[269] of the Janovsky complex to 2,4-dinitrobenzylmethylketone by manganese(III) acetate (yield not stated) and by *N*-oxopiperidinium perchlorate (80%) has been effected.[270]

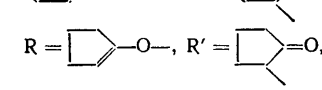
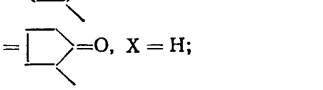


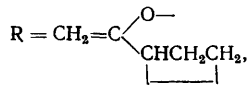
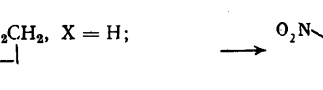
Using as example the σ-complex of *m*-DNB with cyclohexanone anion it was shown that it was possible to apply other oxidising agents such as 2,3-dichloro-5,6-dicyanobenzoquinone (DDBQ), $(NH_4)_2Ce(NO_3)_6$, Br_2 in hexane or $CuBr_2$ in DMF, to the oxidation of complexes of DNB. Systems containing a catalytic amount of CuBr (or $CuBr_2$)/CCl_4 in MeCN also proved to be no less effective. These systems have been used for the oxidation of σ-complexes of

1-X-2,4-DNB obtained *in situ* from organosilicon compounds in the presence of fluoride ion.[222]



R = , R′ = , X = H, Cl, I, Me;

R = , R′ = , X = H;

R = , R′ = , X = H;

R = R′ = CH_2COOEt, X = H;

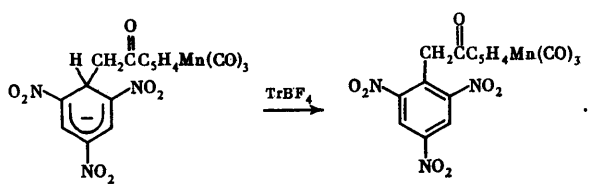
R = R′ = CH_2Ph, X = H;

R = R′ = $CH_2CH{=}CH_2$, X = H.

The effectiveness of the $CuBr/CCl_4$ system was confirmed by an experiment on the oxidation of the isolated and characterised Janovsky complex. The yield of 2,4-dinitrobenzylmethylketone was 80%,[222] i.e. the same as on oxidation with *N*-oxopiperidinium perchlorate.[270]

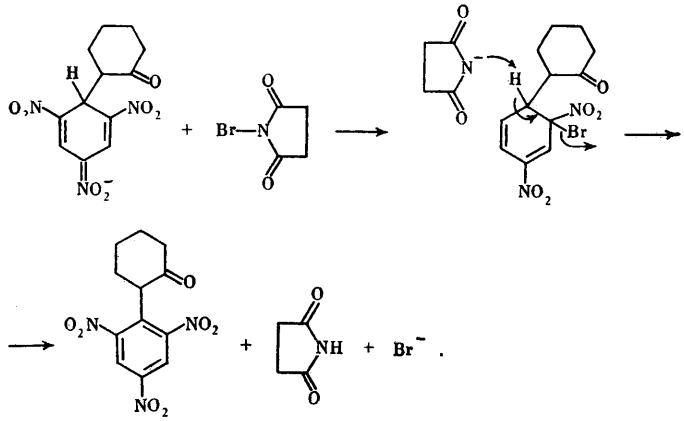
The oxidation of σ-complexes of TNB has been most widely studied. Various organic and inorganic compounds have been proposed as oxidising agents, the use of the latter is convenient and economical due to their availability. In addition the use of inorganic reagents simplifies, as a rule, the isolation of reaction products. The indisputable advantage of organic oxidising agents is their effectiveness. Chloranil, 2,3-dichloro-5,6-dicyanobenzoquinone, tropylium fluoroborate, *N*-oxopiperidinium perchlorate, and *N*-bromosuccinimide (NBS) are used most successfully in the oxidation of σ-complexes.[269–272] $FeCl_3$, $AgNO_3$, $(NH_4)_2Ce(NO_3)_6$, H_2O_2, $Pb(OAc)_4$, and solutions of halogens in water or organic solvents (Py, t-BuOH) are the inorganic reagents applied to the oxidation of σ-complexes.[180,181,271] It should be mentioned that the oxidation of the σ-complex $[TNB.CH_2COMe]^-K^+$ is the only one that has been widely studied. This complex is oxidised in an excellent manner by practically any oxidising agent. In the majority of cases it is seemingly impossible to predict which oxidising agent will prove to be most effective.[221]

It is known that the σ-complex of TNB with acetylcyclopentadienylmanganese tricarbonyl anion is oxidised by tropylium fluoroborate forming the substitution product in 80% yield, however on oxidation with trityl (Tr) fluoroborate a TNB derivative is formed.[178]



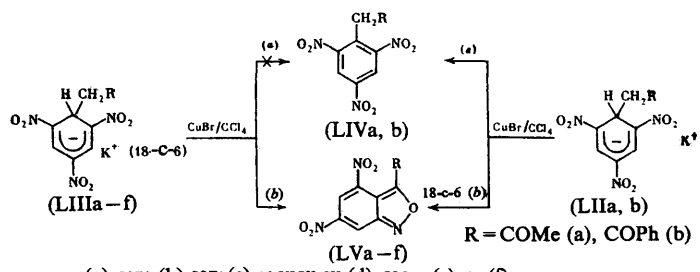
The complexes $[THB.CHal_3]^-$ (Hal = Cl, Br)[128,129] and complexes of TFMSB with R = CH_2COMe, $CH(COOEt)_2$, CH_2NO_2, $CH_2C(O)H$[201] were oxidised by solutions of bromine or chlorine in pyridine or t-BuOH.

NBS has been used successfully as oxidising agent for complexes of TNB with anions of ketones.[221,272] The reaction probably occurs in the following manner.



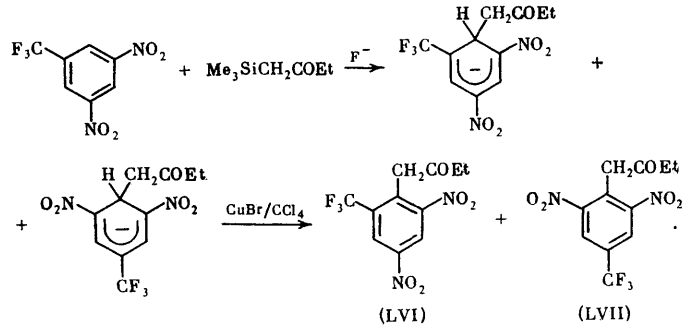
This mechanism was proposed on the basis of data obtained on the oxidation of the σ-complex of TNB with amidine.[20,264] Isoxazoline *N*-oxides are formed on oxidation of bicyclic complexes of TNB and β-dicarbonyl compounds with an excess of NBS.[273] *N*-Bromosuccinimide proved to be an effective oxidising agent for several other σ-complexes such as $[TNB.R]^-K^+$.18-crown-6 ether, where R = $\underline{CH(CH_2)_4CO}$, COMe, COPh, or CH_2Ph.[221] A two fold excess of NBS was required for the oxidation of the σ-complex of TNB (XX) with R = CH_2COOMe when the methyl ester of (2,4,6-trinitrophenyl)bromoacetic acid was formed in 60% yield.[221] To obtain trinitrophenylacetic acid ester $(NH_4)_2Ce(NO_3)_6$ was used as oxidising agent. This reagent also proved to be effective for the oxidation of σ-complexes of TNB with R = C_6F_5, CH_2COEt. When R = All and C≡CPh the use of Cl_2O in CCl_4 has been proposed since the oxidising agents listed above proved to be ineffective.[221]

An unexpected result was obtained on oxidising σ-complexes with the system $CuBr/CCl_4$.[274] On oxidising σ-complexes (LII) where R = CH_2COMe and CH_2COPh substitution products (LIV) were formed. However if the oxidation was carried out in the presence of 18-crown-6 ether (18-c-6) then in place of the expected products (LIV) derivatives of 4,6-dinitrobenzisoxazole (4,6-dinitroanthranil) (LVa–f) were formed (30–70% yield). The result did not depend on whether the reaction was carried out with σ-complexes (LVa–f), whether the content of 18-c-6 was known, or the crown ether was introduced into the reaction mixture simultaneously with $CuBr/CCl_4$ and with complexes (LIIa,b). A necessary condition for such a conversion was the presence of a CH_2R group at the geminal point of the σ-complex.

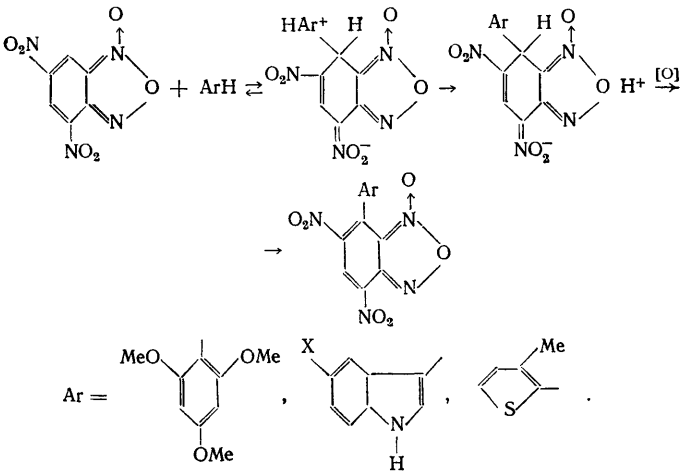


R = COMe (a), COPh (b), $COEt$ (c), $COCHCH_2CH_3$ (d), $COOEt$ (e), Ph (f).

Finally there is one further requirement, viz. the presence of three nitro groups in the aromatic nucleus, for anthranil formation. On oxidation of the σ-complex of 3,5-dinitrobenzotrifluoride only substitution products (LVI) and (LVII) were isolated (1 : 1).

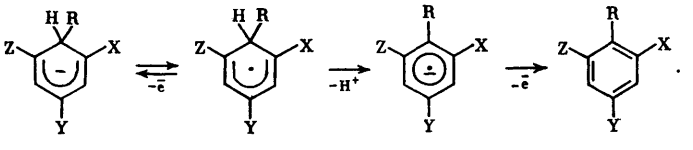


It is interesting that complexes of DNBFX and DNBFZ containing proton as counter ion were capable of spontaneous oxidation in DMSO. This ability is lost on replacement of H^+ by the cation of a metal such as Ag^+.[203]



This observation is all the more astonishing since such complexes are oxidised only by fairly strong oxidising agents such as $KMnO_4$.[203]

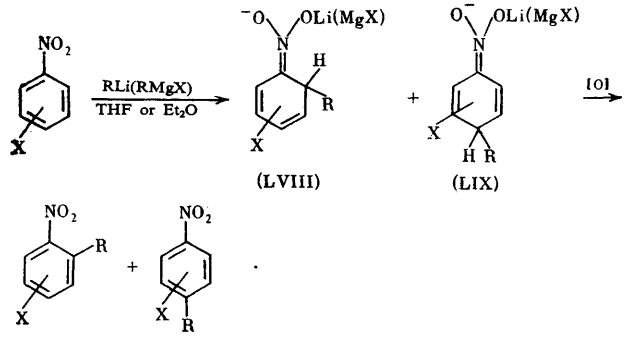
The electrochemical oxidation of acetone complexes of *m*-DNB, TNB and TFMSB and also the complexes of TNB and TFMSB with nitromethane anion has been studied.[177,269,275] It was shown that electrochemical oxidation of σ-complexes proceeds in one irreversible two-electron step and the oxidation potentials of the σ-complexes of TNB (0.82 – 0.92 V) were significantly greater than that of the complex of *m*-DNB (0.33 V) and lower than the oxidation potentials of σ-complexes of TFMSB (1.37 – 1.60 V). The oxidation potentials of σ-complexes increased in the same order as their thermodynamic stabilities. The following scheme was proposed for the oxidation of anionic σ-complexes.



IV. Alkylation of mononitro aromatic compounds

1. Reactions with organometallic compounds and with carbanions

The action of strongly basic organolithium and organomagnesium compounds on nitroarenes usually forms a complex mixture of products of oxidation-reduction reactions and of addition at the nitro group.[5,276–285] It was shown only comparatively recently that this reaction may be successfully applied to the synthesis of various alkyl nitro aromatic compounds if it is carried out at low temperature (–30 to 0 °C) and the reaction mixture is treated with suitable oxidising agents, reducing agents or acids literally a few minutes after mixing the reagents.[286–304] It is evident that unstable σ-complexes like (LVIII) and (LIX) (products of 1,4- and 1,6-conjugated addition) are formed in the reaction of RLi or RMgX with a nitroarene.[289]



The process is reversible if an equimolar ratio of reactants is used, a significant amount of nitro compound is recovered unchanged after the reaction. Best results were obtained using a two fold excess of RMgX. The reversibility of the reaction was also confirmed by the fact that the ratio of adducts (LVIII) and (LIX) changed with time. In the reaction of *o*-nitrotoluene with AlkLi the ratio of products (LVIII) : (LIX) = 1 : 4 after 1 h and 3 : 4 after 5 h.[289,298]

Adducts (LVIII) and (LIX) must be oxidised to obtain nitro alkylaromatic compounds. DDBQ, Br_2, O_2, $Na_2[Fe(CN)_6]$, $KMnO_4$, and $Pb(OAc)_4$ have been used as oxidising agents.[287,289–292] DDBQ is probably the most effective of them, but because of its high cost and poor availability its use is expedient in exceptional cases when a chemoselective oxidising agent not affecting other groups is required.[290,291]

In many cases good results were achieved using $KMnO_4$ in alkaline aqueous acetone.[289] The alkylated derivatives of nitrobenzene, naphthalene and several heterocycles were obtained in this way. $Pb(OAc)_4$ proved to be more effective for the oxidation of adducts of RMgX with polycyclic nitro compounds.[292] It should be mentioned that high yields of oxidation products (70 – 71%) were successfully achieved only for bi- and tricyclic compounds,[287,289,292] i.e. when adducts of type (LVIII) and (LIX) are fairly stable. In the case of nitrobenzene yields did not exceed 50%.[287,289] This is odd, extremely low yields were obtained on alkylating *m*-DNB (5%) and 2,4-dinitrotoluene (12%) (see however pp. 763 – 764).[287]

A comparison has been carried out of the effectiveness of various oxidising agents in relation to the adduct of 2-methyl-1-nitronaphthalene with BuLi (LX) (Table 3).[287] As is evident from the data in Table 3 DDBQ and Br_2 proved to be comparable in effectiveness for this system.

It is interesting that the nitro group is replaced by halogen on oxidation of adducts of type (LVIII) and (LIX) by hypohalites in alkaline medium.[293,294] Thus on treatment of adduct (LXII) with an alkaline solution of hypobromite the dihydro-isomer (LXIII), with bromine and the methyl group in *trans* configuration, is formed in high yield.

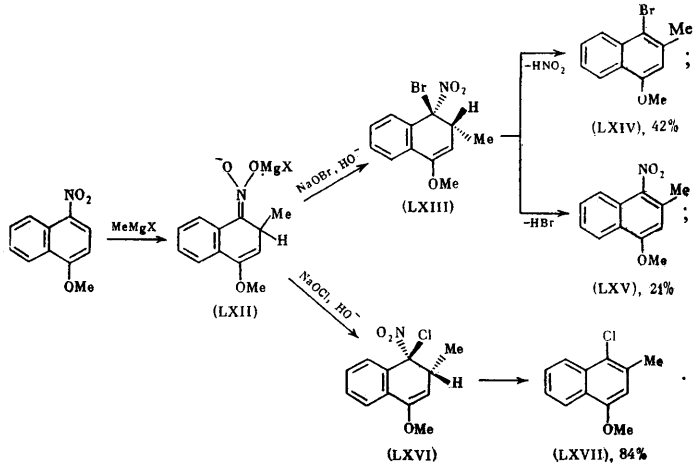
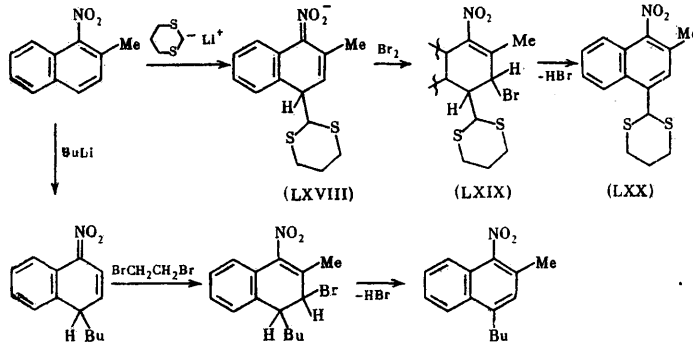


Table 3. Yields of 1-butyl-2-methyl-4-nitronaphthalene (LXI) obtained by the oxidation of adduct (LX) by various oxidising agents.

Oxidant	Solvent	Yield (LXI), %	Oxidant	Solvent	Yield (LXI), %
DDBQ	Ether	75	$Na_3[Fe(CN)_6]$	Ether	40
Br_2	Ether	70	$BrCH_2CH_2Br$	Hexane	26
O_2	Hexane	30			

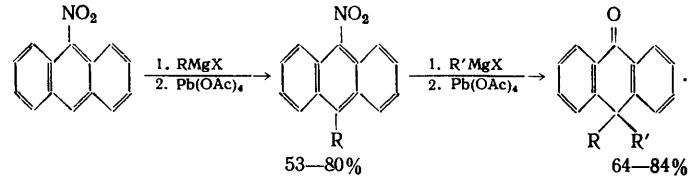
The adduct (LXIII) eliminates HNO_2 in alkaline medium (E_2 type process). The *trans* elimination occurs more readily than *cis* elimination (HBr) which also determines the predominant formation of product (LXIV) [ratio (LXIV):(LXV) = 2:1].[288,294] On replacing bromine by the poorer leaving group chlorine, i.e. on oxidising compound (LXII) with hypochlorite, the chloro derivative (LXVII) was formed exclusively.[293,294] The latter reaction was used for the synthesis of several chloro alkylarenes.[293]

It has been proposed that bromination of the nucleus occurs, albeit partially, on oxidation of adducts of type (LVIII) and (LIX) with bromine or dibromoethane. Subsequently aromatisation of the intermediate compound takes place by elimination of HBr.[287] In reality compound (LXIX) was isolated in 50% yield on oxidation of adduct (LXVIII) with bromine. On treatment with Et_3N, HBr was eliminated and (LXIX) was converted into the oxidation product (LXX).

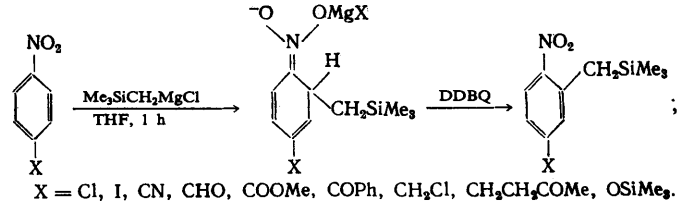


Other valuable compounds may be obtained from adducts (LVIII) and (LIX), such as nitroso alkylarenes (by treatment with BF_3 or concentrated HCl),[290,295–297] amines and hydroxylamines [by the action of an excess of RMgX and catalytic amounts of CuI or phosphorus(III) compounds].[298,299] A good method of obtaining arylamines is the reduction of adducts (LVIII) and (LIX) with hydrides ($LiAlH_4$ or $NaBH_4$) in the presence of catalytic amounts of Pd/C (–30 °C, ~20 min, 30–75% yield).[300]

It should be mentioned that the reaction of RM with nitroarenes is extremely regioselective. When a substituent such as OMe, OAr, SMe, SPh, Cl or F is present in the *ortho* or *para* position of a nitroarene an alkyl group R will enter almost exclusively at the unsubstituted position.[288,290] However when alkyl substituents are present a mixture of 1,4- and 1,6-addition products are formed in the ratio 2:1.[288,297] This special feature may be used for alkylating 1-R-2-naphthalenes at the C-1 atom[301] or for the two step synthesis of 10-R-10-R'-anthrones from 9-nitroanthracene.[292]



The reaction of nitroarenes with Me_3SiCH_2MgCl has been proposed for the synthesis of organosilicon compounds of the benzyl type.[302,303] The high regio- and chemoselectivity of this reaction enables the preparation of benzyl compounds of silicon containing such substituents as halogens, carbonyl and cyano groups.[303] Yields of products were 53–80%.

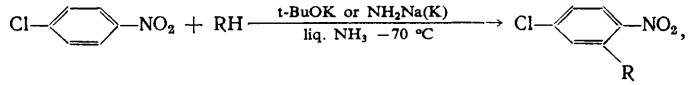


X = Cl, I, CN, CHO, COOMe, COPh, CH_2Cl, CH_2CH_2COMe, $OSiMe_3$.

Reaction in this case was carried out with a stoichiometric amount of RMgX and, as a rule, at low temperature (–70 to 0 °C). DDBQ proved to be the best oxidising agent, however oxidation has been carried out with $KMnO_4$.[302] The same high yields of organosilicon compounds were obtained in the reaction of Me_3SiCH_2MgCl with homo- and heterocyclic nitroaromatic compounds of naphthalene, quinoline, indole and anthracene.[303]

In contrast to alkyl magnesium chloride, allyl magnesium chloride gives adducts with 1,2-addition at the nitro group with $ArNO_2$, treatment of which *in situ* with $LiAlH_4$ in the presence of catalytic amounts of Pd/C leads to *N*-allyl-*N*-arylhydroxylamines or *N*-allylanilines.[304]

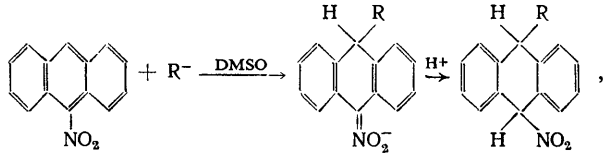
As already mentioned the reaction of mononitroarenes is reversible even with RLi or RMgX which is all the more remarkable since nitroarenes react with fairly stable carbanions (pK_a 20–12 for the corresponding CH-acid) in liquid NH_3.[305-306]



R = CH_2COMe, CH_2COBu-t, CH_2COPh, CH_2CN, CH_2COOBu-t.

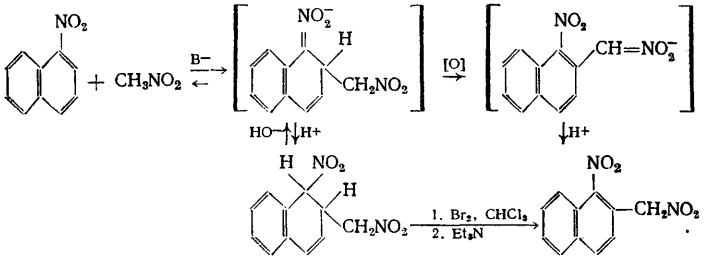
The oxidising agent is evidently partially *n*-$NO_2C_6H_4Cl$ itself and partially O_2 since the yields of substitution products (22–62%) were reduced on carrying out the reaction in an inert atmosphere.

It is possible to isolate the corresponding dihydro derivatives in good yield in the case of 1-nitronaphthalene and 9-nitroanthracene.[307]



R=CH $(COOEt)_2$, C (Me) $(COOEt)_2$, CH $(CN)_2$, Me_2CNO_2.

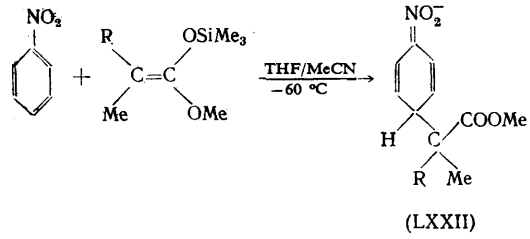
Nitromethane reacts with 1-nitronaphthalene in DMSO in the presence of NaOH forming an anionic σ-complex which may be oxidised directly or through the step of obtaining the dihydro derivative.



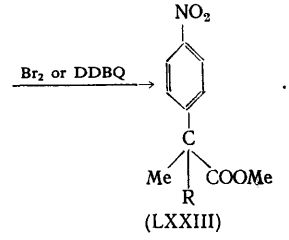
Monocyclic arenes do not react under these conditions.[308]

Such reactive organosilicon compounds as silylenol ethers and silyl ketene acetals and also *C*-silylated methyl acetate react successfully with mononitroarenes in the presence of F ion.[309,310] The salt *tris*-(dimethylamino)sulphonium difluorotrimethylsiliconate $(Et_2N)_3S^+Me_3SiF_2^-$, which is soluble in organic solvents, served as the source of F ion. The yields of products were reduced on using Bu_4NF.[310]

Adducts of 1,4- and 1,6-addition of $RSiMe_3$ were established in the reaction by PMR spectroscopy at –60 °C. Thus ketenacetal (LXXI) gives adduct (LXXII) with nitrobenzene.[310]

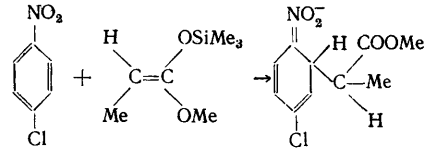


(LXXII)



(LXXIII)

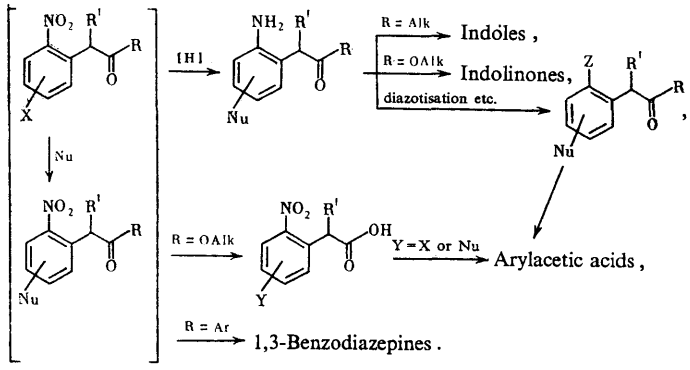
Adduct (LXXV) was established in the reaction of ketenacetal (LXXIV) with 4-chloronitrobenzene.[310]



(LXXIV) (LXXV)

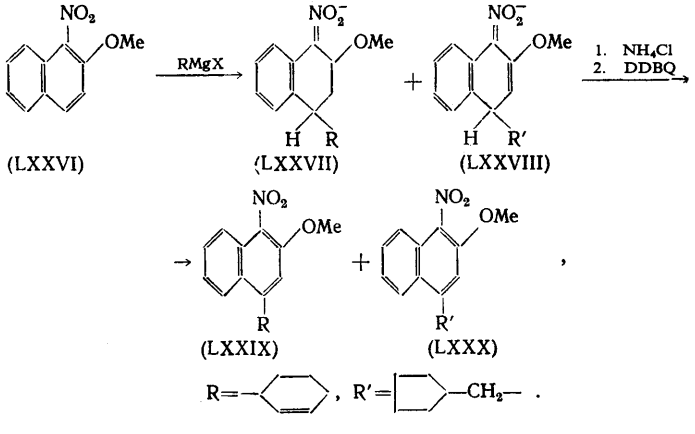
It was noted that alkali metal enolates did not add to nitroarenes under these conditions.[310]

The use of silyl ketene acetals, silylenol ethers and trimethylsilylacetic ester enables synthesis of α-nitroarylated ketones and ethers which are proposed for use in the synthesis of indoles, indolinones and arylacetic acids with various substituents.[311]

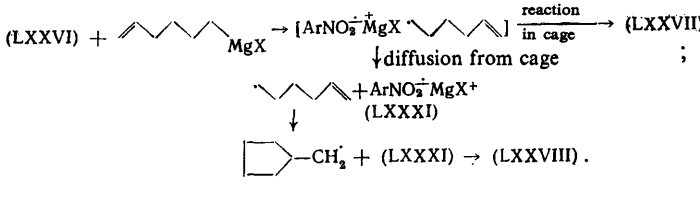


The principles discovered when studying the reaction of nitroarenes with Grignard reagents[288] and $RSiMe_3$ [309,310] are extremely complex. The regiochemistry of the addition is controlled by the size of the organosilicon compound. For example compound (LXXIII) is a single isomer in the reaction shown above. With less sterically hindered silyl ketene acetals such as Me_3SiCH_3COOMe the *ortho*-isomer is formed predominantly. In reactions of nitroarenes with $RSiMe_3$, as in reactions with RMgX, the halogen atom in the nucleus is not affected.[288,310] In the case of arenes with bi- and tricyclic nuclei it is possible to isolate the corresponding dihydro derivatives by treatment of the reaction mixture with acid. On oxidising the adducts with bromine dihydro compounds like (LXIX), which have a bromine atom in the nucleus, were detected.[310]

It is well known that the formation of anion radicals (AR) is repeatedly observed in reactions of nitroarenes with $RMgX$[284] or carbanions.[312] Furthermore, certain carbanions such as diphenylacetonitrile,[54] diphenylallyl,[313] fluorenyl[314,315] and others are oxidised by nitrobenzene to dimers, i.e. under definite conditions the reaction of $ArNO_2$ with RM may proceed by a single-electron-transfer (*SET*) mechanism. The problem then arises as to whether adducts (LVIII) and (LIX) are formed by the usual heterolytic route or by *SET*. The reaction of 2-methoxy-1-nitronaphthalene with hexen-5-ylmagnesium bromide was selected as a test for the existence of the *SET* mechanism.[288,291] [It is known that the hexen-5-yl radical rapidly cyclises at room temperature into the cyclopentylmethyl radical ($K \sim 10^5$ sec^{-1})[316]]. After adding DDBQ to the reaction mixture two alkylnitro compounds (LXXIX) and (LXXX) were isolated in the ratio 64:36 (overall yield 78%).



This result afforded the conclusion[288,291] that the reaction proceeded according to the radical route by at least 36%, but it is quite probable that the whole process is radical.

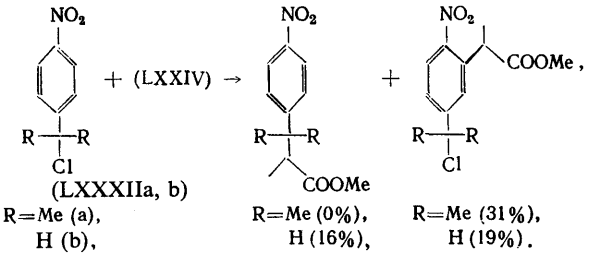


The order of reactivities of various RMgX [in reactions with nitroarene (LXXVI)] also supports the radical mechanism.

$$\text{iso-PrMgBr} > PhCH_2MgBr \simeq EtMgBr > MeMgBr.$$

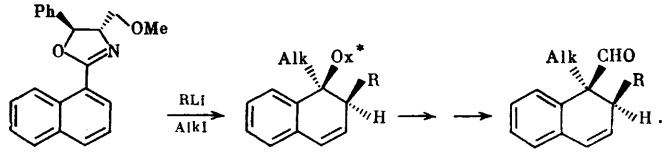
The order is determined by the ease of oxidation.[291,317]

Certain authors[310] considered the reaction of NO_2Ar with organosilicon compounds to be a heterolytic process. Their reasoning was as follows. Firstly, halogen on the nucleus is not affected in these reactions, if AR are formed then elimination of halogen must be observed. Secondly, in the reaction of (LXXIV) with 4-nitrocumyl chloride (LXXXIIa) replacement of chlorine did not occur and dicumyl or the dimer of the enolate were not detected.



However, replacement of chlorine takes place in the case of the unhindered *n*-$NO_2C_6H_4CH_2Cl$ (LXXXIIb). In addition 1-cyclopropyl-4-nitrobenzene reacts with (LXXIV) without fission of the cyclopropane ring. Finally, as already mentioned above, the formation of adducts (LXXII) and (LXXV) was detected by PMR spectroscopy and at –60 °C the signals in the PMR spectra were not broadened.[310]

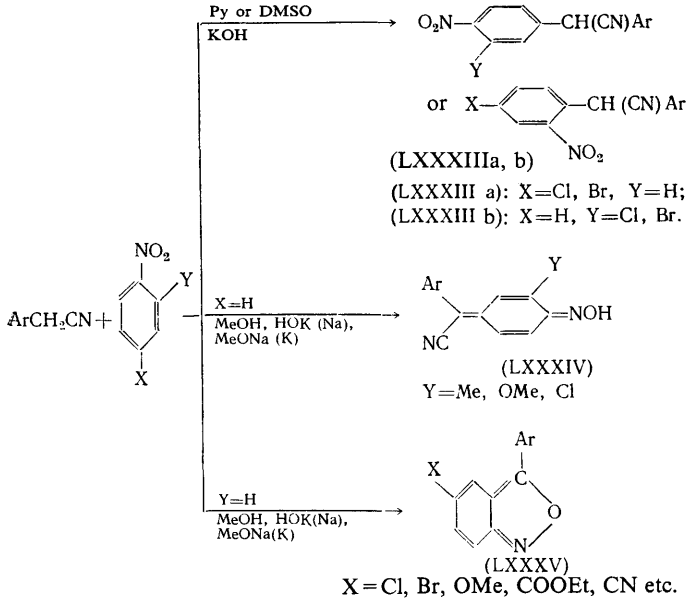
Usually the alkylation reactions described above are possible only for nitroarenes, the presence of such substituents as CF_3, CN or COR proved to be insufficient to activate the arene. However it was found comparatively recently that similar reactions (with RLi or RMgX) also occur on activation of the arene nucleus with an oxazoline group (see also p. 754). Products of *trans*-addition were formed in high yield on treating the adducts obtained with various electrophiles.[318–321]



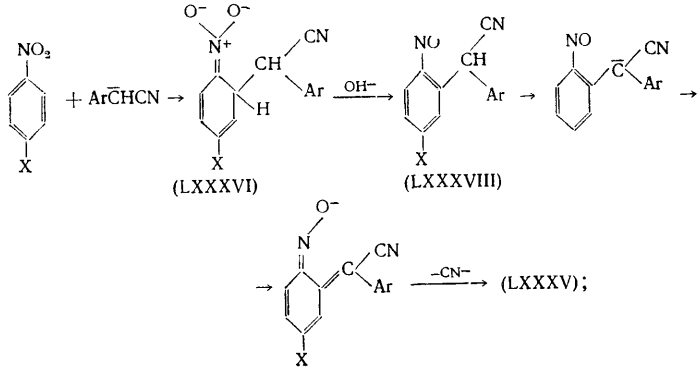
Such 'tandem addition' of RLi, RMgX and carbon-containing electrophiles has been described for (1-naphthyl)- and (2-naphthyl)-oxazolines.[318,319] Various proton sources were also used as electrophiles.[319–321]

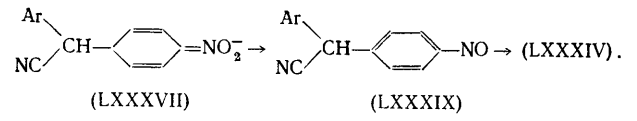
Adducts formed by addition of carbanions to nitro compounds (LVIII) and (LIX) are capable in certain cases of further spontaneous conversion which may be considered as oxidation-reduction processes with the participation of the NO_2 group. Thus over many years the steady attention of investigators has been attracted by the reaction of phenylacetonitrile and its substituted derivatives with nitroarenes which occasionally leads to the formation of unusual products.[54,322–333] The interaction of $ArCH_2CN$ with halonitrobenzenes may proceed according to three

different routes depending on the nature of the nitrocompound and the solvent.[54,322–333]



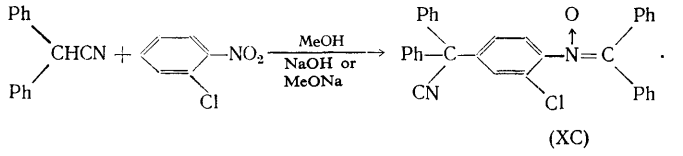
As already mentioned, replacement of halogen was observed in aprotic dipolar solvents like DMSO or Py.[54,322,323] However the situation changes sharply on replacing an aprotic solvent by methanol. In this case derivatives of quinonoxime (LXXXIV) (the oxime of 4-α-cyanoarylidene-2,5-cyclohexadien-1-one) are formed if the *para* position in the nitroarene is free.[324–328] This reaction route is effected with the selfsame variety of acetonitrile derivatives (Ar is homo- or heteroaryl) and various nitroarenes, including bicyclic and heterocyclic. When the *para* position is blocked and the *ortho* position free 3-arylanthranils (LXXXV) are formed which are used for the synthesis of 9-acridinone, acridine, benzophenones and 1,4-benzodiazepines.[323,329–331,334] The formation of both compounds (LXXXIV) and (LXXXV) may be explained within the framework of one or the other mechanism, comprising attack of the carbanion at the *ortho* or *para* position of the benzene ring [formation of adducts (LXXXVI) and (LXXXVII)], elimination of hydroxyl ion which leads to nitroso compounds (LXXXVIII) and (LXXXIX), intramolecular cyclisation of *o*-nitro compound (LXXXVIII) to anthranil (LXXXV) or isomerisation of the *p*-nitro compound (LXXXIX) to quinonoxime (LXXXIV).[54,323,325]



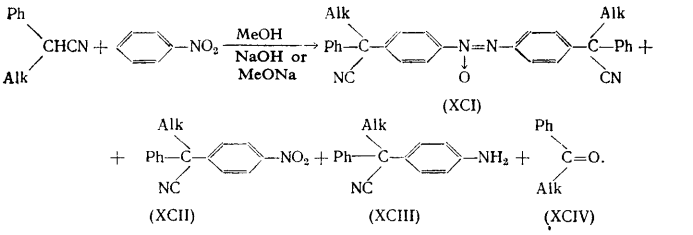


Regrettably it is still unclear in what way the conversion of (LXXXVI) →(LXXXVIII) or (LXXXVII)→(LXXXIX) occurs. The strong influence of solvent on the route of reaction is also not understood.

Phenylacetonitriles substituted in the α-position are evidently unable to give products like (LXXXIV) and (LXXXV). Diphenylacetonitrile forms nitrone (XC) in high yield on reaction with a nitroarene with a free *para* position in the benzene ring.[54,323,332–334]



Under these conditions α-alkylphenylacetonitriles gives a complex mixture of compounds (XCI)–(XCIV) with $PhNO_2$ among which is the product of replacement of hydride ion.[54,332]



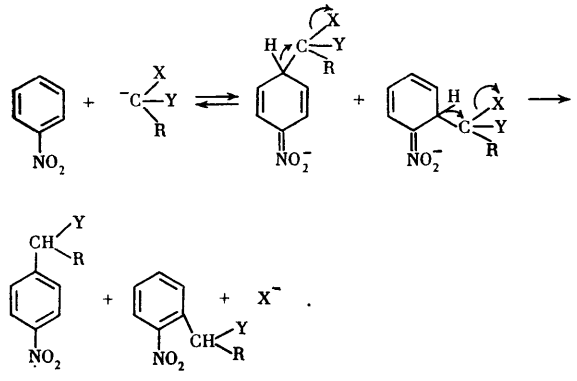
The presence of amine (XCIII) in the reaction mixture probably indicates that 1 mole of nitro compound behaves as an oxidising agent in relation to an adduct like (LXXXVII). The formation of all the remaining products is readily explained by subsequent conversions of nitroso compounds.[54,332,333] It is noted that in weakly polar solvents like benzene the anion of diphenylacetonitrile is oxidised by nitroarenes to the dimer.[54,332]

2. Vicarious nucleophilic substitution of hydrogen

The alkylation of nitroaromatic compounds by carbanions has been described above. In these reactions removal of hydride ion from the intermediate complex is effected by an oxidising agent. The oxidising agent is introduced into the reaction mixture specially or the initial nitroarene fulfils this role, in this way an intra- or intermolecular oxidation of the σ-complex occurs.

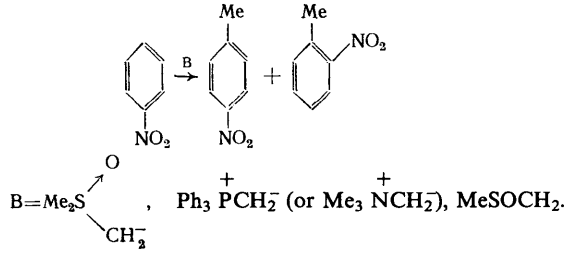
Another route for converting adducts (LVIII) and (LIX) into alkylnitroarenes has emerged using carbanions containing 'good' leaving groups. The essence of the reaction is that under the action of the carbanion a hydrogen atom in the position *ortho* or *para* to the nitro group of the nitroarene is replaced. The substituent X acts as a 'vicarious' leaving group and Makosza and collaborators

have proposed the general name of vicarious nucleophilic substitution (VNS) for the whole process.[335–339]

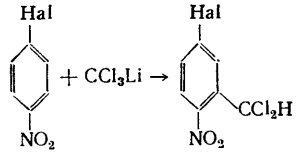


X is a leaving group: Cl, Br, PhS, PhO, $R_2NC(S)S$, etc.; Y is a group stabilising the carbanion: SO_2Ar, SO_2NR_2, SO_2OR, SOAr, CN, COOR, $CONR_2$, $P(O)Ph_2$, $P(O)(OEt)_2$, etc.; R = H, Alk, Ar. In spite of the fact that individual examples of similar reactions were known previously,[340–346] only the systematic work of Makosza and collaborators has attracted general attention to like reactions and the study of them has proceeded independently.

It is known that methylation of nitrobenzene and certain of its substituted derivatives occurs under the action of methylids of sulphur, phosphorus or of dimethylsulphinyl carbanion.[340,341]



The reaction of halonitrobenzenes with CCl_3Li, which may serve as a method of dichloromethylating and formylating nitroarenes, should also be considered as a VNS.[342,347]

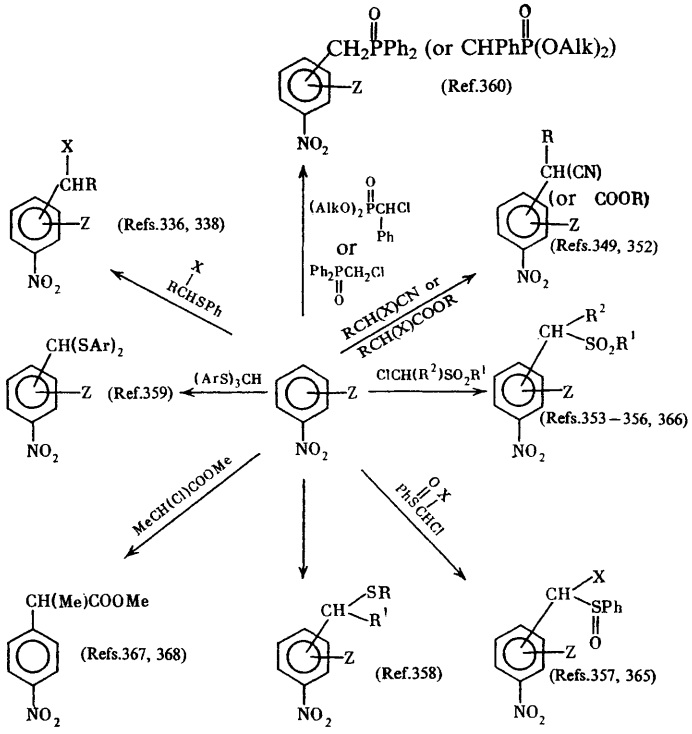


The possibility of nucleophilic substitution of hydrogen in nitroheteroarenes has been shown.[343–346]

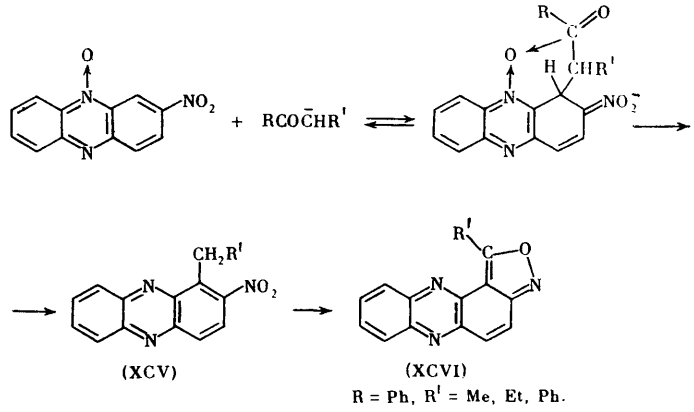
In the general case, as shown by Makosza and collaborators,[336–339] for the successful achievement of the VNS reaction, it is necessary that the carbanions are sufficiently stable and do not react with the CH-acids from which they were formed. This is attained by an appropriate combination of groups X and Y. However when X = Hal not many CH-acids satisfy this requirement consequently CH-acids are used which contain poorer leaving groups such as PhS, PhO, $R_2NC(S)S$, etc.[336–339]

The choice of base and solvent is another important requirement. Such systems as NaOH(KOH)/DMSO or NH_3, NaOH/DMF, R_4NOH/PhH(PhCl) proved to be most suitable. This means that solvent-separated ion pairs or free ions possess the greatest reactivity. Under such conditions the VNS reaction enables the introduction of various α-functionalised alkyl groups into the *ortho* and *para* positions of nitro aromatic compounds.[335–368] It should be mentioned that the products of VNS contain at least one acid hydrogen atom in the α-position, consequently they may react with other electrophiles such as RHal, RCHO, etc. (Scheme 3).[347]

Scheme 3



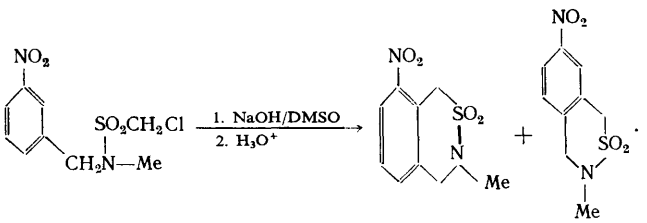
A more complex case of the VNS reaction has been described[346] in which the leaving group is carboxylate ($RCOO^-$). Various products are obtained depending on the nature of the ketone which reacts with 2-nitrophenazine-10-*N*-oxide. These include the normal products of substitution of hydride ion (XCV), anthranils (XCVI) and other more complex compounds (see previous section).[346]



(XCV) (XCVI)

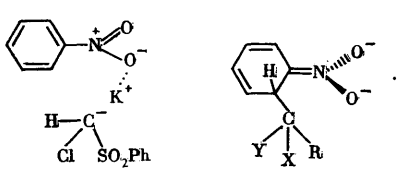
R = Ph, R' = Me, Et, Ph.

The intramolecular VNS process may serve as a source of various isocyclic and heterocyclic compounds.[369]

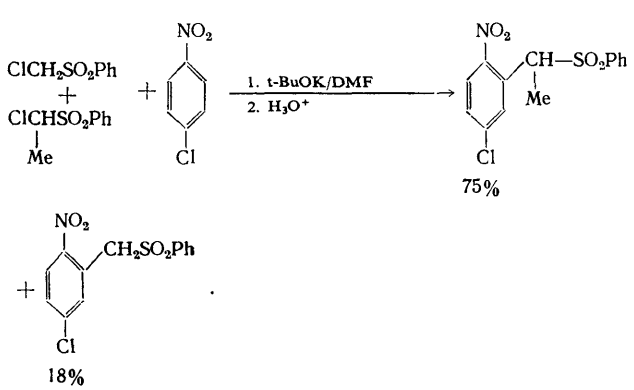


The intramolecular VNS reaction is used for the synthesis of tetracycline derivatives.[370]

The VNS reaction is distinguished by several special features. Tertiary carbanions usually replace a hydrogen atom in the *para* position of the nitroarene,[337,338,357] although there are several exceptions.[349,357] A mixture of *ortho* and *para* isomers, the ratio of which depends on the size of groups X and Y, is formed from secondary carbanions when using DMSO, DMF or liquid NH_3 as solvent.[349,350] On the other hand, the application of the THF/t-BuOK system enables selective replacement of hydrogen in the *ortho* position to the nitro group.[351,352,356] This is explained by the fact that the carbanions are mainly in the form of contact ion pairs or aggregates with the potassium ion in THF in difference to DMSO. The potassium cation, forming a bond with negatively charged oxygen in the NO_2 group, directs the associated carbanion to the *ortho* position.[352,356]



However under definite conditions (DMF, t-BuOK, –40 to –30 °C)¶ tertiary carbanions like α-chloroalkylphenylsulphone also readily substitute hydrogen in the *ortho* position of a nitroarene. Furthermore in competing reactions of tertiary and secondary carbanions the former react at the higher rate.[366]



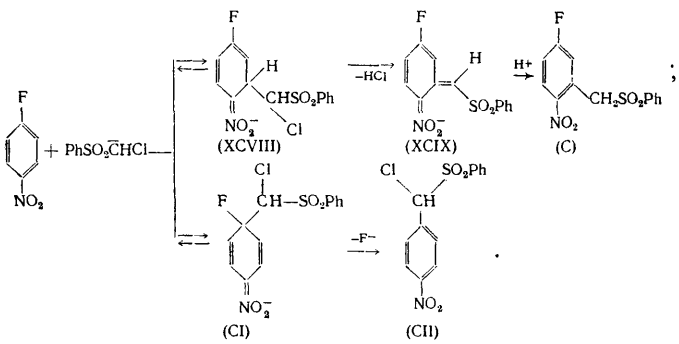
¶Tertiary carbanions and *o*-nitrobenzyl carbanions of the corresponding products are unstable at higher temperatures.[367]

Of the two possible *ortho* isomers the most hindered (1,2,3 isomer) is formed for the majority of 3-substituted nitrobenzenes.[353,356] This same special feature of the reaction was also observed in the methylation of nitroarenes by ylids.[342] Thus by changing the solvent and by varying groups R, X and Y in the carbanion it is possible to change the regioselectivity of the VNS reaction in an effective manner.

The VNS reaction is distinguished by its special features for naphthalenes.[365] 1-Nitronaphthalene gives a mixture of 2- and 4-substituted products [in reactions with $ClCH(R^2)SO_2R^1$ the ratio of 2-isomer : 4-isomer = 10 : 1]. The preference for attack by the carbanion at position 2 is comprehensible on considering the mesomeric structures of the appropriate σ-adducts. Reaction of 2-nitronaphthalene with secondary carbanions occurs exclusively at position 1. This tendency was so large that no VNS reaction occurred on blocking position 1 with a MeO group but a nucleophilic aromatic substitution of the MeO group took place. No reaction occurred with tertiary carbanions (such as α-chloropropyl-p-tolylsulphone).[365]

Donor groups (NMe_2, Me, OR) and even negatively charged groups of the COO^- type proved to have no significant influence on the VNS reaction.[355,361] Mononitrophenoxides did not undergo a VNS reaction, however this reaction is possible for di- and trinitrophenoxides.[362] In this case it probably occurs as a nucleophilic addition to the cyclohexadienenitronate system.[362] We also note that VNS reactions are known for DNB and TNB in which it is possible to substitute two and three hydrogen atoms respectively.[362]

Like the reactions with RLi, RMgX or $RSiMe_3$ vicarious nucleophilic substitution may be used for alkylating halogen-substituted nitrobenzenes since the rate of substituting hydrogen is far greater than that for Cl, Br or I. Replacement of both hydrogen and fluorine or nitro group depending on the conditions was observed in *o*- and *p*-fluoronitrobenzenes and *p*-dinitrobenzene.[336–339,363,368] An interesting dependence of reaction route on base concentration has been discovered.[363] On interacting *p*-fluoronitrobenzene with chloromethylphenylsulphone (XCVII) at a ratio (XCVII)/t-BuOK = 2 the formation of both possible products (C) and (CII) was observed but with a four fold excess of t-BuOK the product of VNS (C) was obtained exclusively.



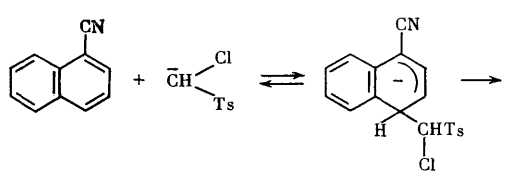
This dependence is displayed even more clearly in the competing reaction of phenoxyphenylacetonitrile (CV) with a mixture of NO_2Ph and *n*-$FC_6H_4NO_2$. At a ratio (CV)/t-BuOK equal to 2 approximately identical amounts of the VNS product and that from fluoride

ion substitution were obtained. At a ratio (CV)/t-BuOK = 4 practically only the product of hydrogen substitution was obtained. From this it follows that addition of carbanion to an unsubstituted carbon atom [adduct (XCVIII)] occurs more rapidly than formation of an adduct containing a fluorine atom at the geminal node (CI).[339,363]

It is certain that the VNS reaction includes the reversible formation of an intermediate σ-complex. It is assumed that its conversion into the reaction product may occur either by removal of the leaving group X from the carbanion with a simultaneous 1,2-hydride shift or by base catalysed elimination of HX.[336–339,363] The observed dependence of the reaction route on base concentration and also isotope effects K_H/K_D found in several cases,[339,363,368] indicate that the second mechanism is true. The mechanism of VNS therefore includes a rapid, reversible σ-complex formation and subsequent slow elimination of HX. The rate of elimination must, nonetheless, be more than the rate of addition of carbanion to the carbon bonded to halogen.[339]

Regarding the mechanism of formation of the σ-complex, the authors regard this reaction to be ionic.[339] The clearly expressed influence of solvation of the cation on the route of addition of carbanion to NO_2Ar indicates this. In addition cyclisation products were not detected in the reaction of 1-chloro-5-hexenylphenylsulphone with nitroarenes[339] (cf. addition reactions of RMgX to NO_2Ar[285]).

In conclusion we note that the VNS reaction, like the alkylation reaction described in Chapter IV, Section 1, is only possible for nitroaromatic compounds. Arenes with less strongly electron-accepting substituents in the nucleus, as a rule, do not take part in this reaction. The reaction of 1-cyanonaphthalene with chloromethyl-4-tolylsulphone leading to *bis*-cyclopropane derivative (CIV) proved to be even more unexpected.[364]



(CIII) (CIV)

This result is probably explained by addition of carbanion at the C-4 atom with subsequent intramolecular nucleophilic substitution which leads to the monoannulated product (CIII). The latter, being an active Michael acceptor, adds a second molecule of carbanion finally forming (CIV).[364]

We note that vicarious nucleophilic substitution has been illuminated in more detail in a review.[371]

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