Translated from *Uspekhi Khimii* 60 134–168 (1991) U.D.C. 547.567

Nucleophilic reactions of quinones

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ABSTRACT. **Nucleophilic addition to, and substitution of, quinones have been systematically reviewed. Particular attention has been paid to establishing general trends in reactivity in the light of our present-day understanding of mechanistic chemistry.**

The bibliography contains 188 references.

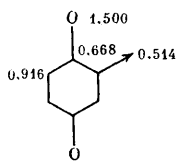
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I. Introduction

Quinones are widely distributed in nature and are produced industrially in all the developing countries. Historically the first, and still the major, application of quinones has been in the dye industry. At the present time, quinoidal compounds are used as dyes and luminophores in photography and electrophotography, in optical quantum generators (lasers), liquid crystalline and photochromic materials, and as scintillators.[1–5] However, the value of quinones is not restricted to dye chemistry. Our knowledge of the biological activity of quinones has developed enormously, not only with the discovery of the vitamin K group, but also with the preparation of drugs, herbicides, fungicides, and plant-growth regulators.[6–16] Quinones have also been used as analytical reagents, polymer modifiers, photoresistors, and catalysts.[17–21] Halogeno- and cyano-quinones are used in organic synthesis as indispensable dehydrogenating agents, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone being one of the most powerful organic oxidants.[22] No doubt applications of quinones will become even more widespread.

LCAO–MO calculations for 1,4-benzoquinone have shown that the distribution of π-electron density is very uneven,[23] as depicted below.

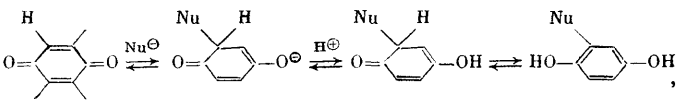


The wide variation in the electron density of quinones explains the broad spectrum of activity of this class of compound. In fact, quinones participate in an enormous number of homolytic and heterolytic reactions. This review is devoted to the most interesting of the heterolytic processes; nucleophilic reactions, which exemplify the rich synthetic potential of quinones. Electrophilic reactions are less varied, being limited to the interaction of quinones with hydrogen- and metal-containing reducing agents to give hydroquinones or semi-quinoidal complexes.[24–37]

In recent reviews devoted to various aspects of the chemistry and use of quinones, there is a notable absence of information on the nucleophilic and electrophilic reactions of quinones.[38–43] We have sought in this review to make good this deficiency. Data are presented here on the reactions of quinones with nucleophilic reagents in the light of our present-day understanding of mechanistic chemistry.

II. Nucleophilic addition to quinones

The general scheme of nucleophilic addition to 1,4-quinones is presented below (1,2-quinones interacting in a similar way).



$Nu^{\ominus}$ – nucleophile.

The final step in the scheme is shown as a reversible process. However, as a rule it is irreversible since it leads to the formation of a stable aromatic system. Here, a proton is depicted as the electrophile. With other electrophiles, the overall scheme is the same; only the detail changes.

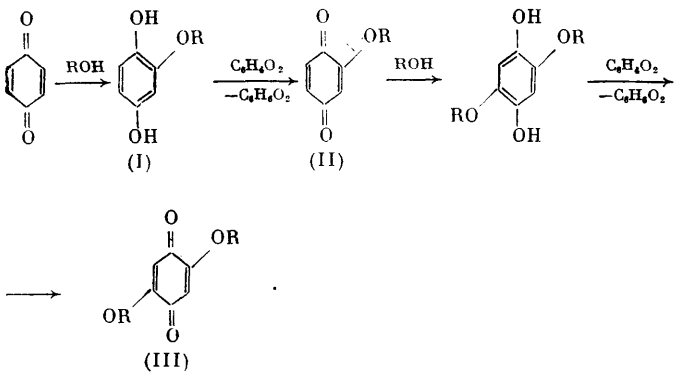
From molecular orbital calculations, the coefficients for the higher, occupied and lower, unfilled molecular orbitals have been determined for substituted 1,4-benzoquinones and 1,4-naphthoquinones. From this data, rules have been established for the orientating effects of substituents on nucleophilic addition. Thus, for 2-substituted 1,4-benzoquinones, the order of reactivity of ring positions is 5 > 2 > 6 for donor substituents, and 3 > 6 > 5 for acceptor or unsaturated substituents. The 2-position of 1,4-naphthoquinone is activated by donor substituents at C_2 and C_6 and by acceptor and unsaturated substituents of C_5. The 3-position activates donor substituents at C_5; an *anti*-5-OH group acts as a donor, while a *syn*-5-OH group acts as an acceptor.[44]

The calculations are generally in accord with resonance theory, as will be seen later, and are confirmed by experimental data except in the case of nucleophilic addition to carbon without a donor substituent.

1. Reactions with *O*-nucleophiles

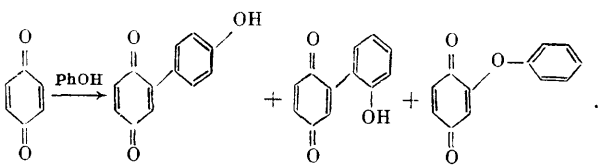
Normally, direct addition of water to quinones to give an adduct is not possible; one exception has been reported but it has no preparative value.[45] Primary alcohols react with quinones only in the presence of catalysts: zinc, cadmium, calcium and magnesium.

However, the highly active 2-acetyl-1,4-benzoquinone does react without a catalyst. Reaction involves initial nucleophilic addition of the alcohol to the quinone with formation of alkoxyhydroquinone (I); this is then oxidised by the starting quinone to alkoxyquinone (II). A second molecule of the alcohol adds to the latter to give the corresponding 2,5-dialkoxy-1,4-benzoquinone (III) as final product.



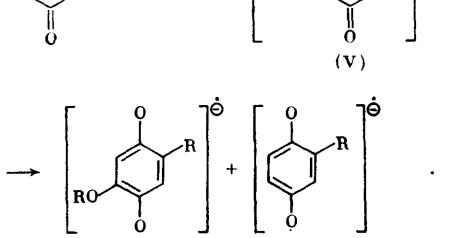
(I) (II) (III)

There are isolated examples of the reaction of secondary alcohols with quinones, but tertiary alcohols are unreactive. C-Arylated quinones are generally obtained by reaction of phenols with quinones. The yield of aryloxy derivatives (IV) is no more than 5%.[45]



(IV)

A kinetic study of the reaction of 1,4-quinones with alkoxide ion in alcoholic media has shown that the process involves initial formation of a charge-transfer complex (V) between the 1,4-quinone and alkoxide ion, followed by its conversion into quinol radical anions, the ratio of which depends on the nature of the alkoxide ion, the substituent on the 1,4-quinone ring, and the medium.[46]



(V)

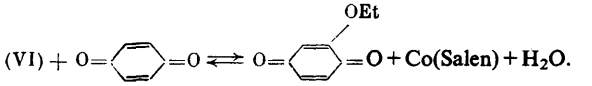
There is virtually no reaction of 1,4-benzoquinone with ethanol in the absence of catalyst. Reaction is facile in the presence of bis(*N*,*N*-salicylideneethylenediaminato)cobalt, Co(Salen), and oxygen.

It is thought that reaction involves three stages:

$$2\text{Co(Salen)} + O_2 \rightleftarrows 2\text{Co(Salen)}-O,$$

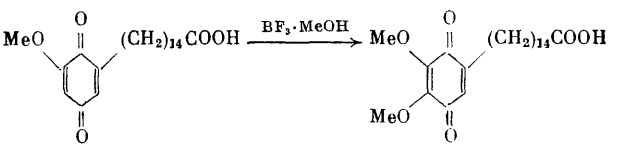
$$\text{Co(Salen)}-O + \text{EtOH} \rightleftarrows \text{EtOH}-\text{Co(Salen)}-O,$$

(VI)

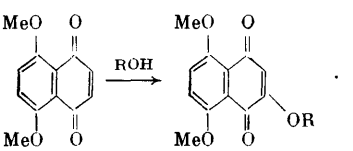


The last step is rate-determining. It has been suggested that Co(Salen) forms a 2:1 complex with O_2, existing as a dimer (with a Co–O–O–Co bond) in the solid state and in alcoholic media. The formation of complex (VI) requires cleavage of the O–O bond by attack of an alcohol molecule on cobalt. Increase in the size of the alcohol molecule hinders this cleavage for steric reasons, which explains the reduction is yield. ^{1}H NMR spectroscopic data indicated that complex formation between Co(Salen) and alcohols is a reversible process. Reaction is inhibited by the addition of chloroform [which forms a simple adduct with Co(Salen)] or benzene [which also associates with Co(Salen)], resulting in elimination of oxygen.[47]

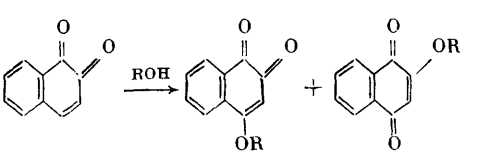
BF_3 may be used as catalyst for the reaction of quinones with alcohols. Methoxylation of substituted 1,4-benzoquinones takes place in the presence of BF_3.MeOH complex.[48]



1,4-Naphthoquinones with donor substituents in the 5 and 8 position react with alcohols to give 2-alkoxy derivatives in the presence of sulphuric acid and a little iron sulphate as catalyst.[49]



1,2-Quinones react with alcohols in the same way as 1,4-quinones in the presence of catalyst. A study has been made of the reaction of 1,2-napthoquinones with alcohols in the presence of sodium iodate and a metal salt ($CoCl_2$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $LaCl_3.7H_2O$, $CeCl_3.7H_2O$).[50] The yield of the resulting 4-alkoxy-1,2-naphthoquinone (VII) increases according to the sequence of reagents shown, being 3% with $CoCl_2$ and 79% with $CeCl_2.7H_2O$. Quinone (VII) is not formed in the absence of catalyst. 2-Alkoxy-1,4-naphthoquinones (VIII) are formed in addition to (VII) on prolonging the reaction and increasing the temperature.



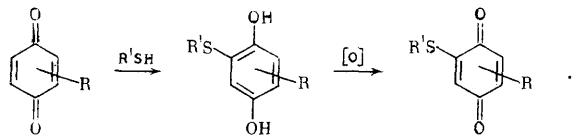
(VII) (VIII)

Alcoholysis of acenaphthoquinone and the related *o*-pleiadienoquinone leads to the formation of the corresponding quinone ketals.[51]

2. Reactions with *S*-nucleophiles

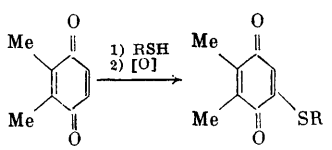
(a) With thiols

Thiols and thiophenols react with 1,4-quinones to give 1,4-adducts (IX), which, in the course of reaction, are oxidised by air or by the starting quinone to provide the corresponding alkylthio- or arylthioquinones (X).



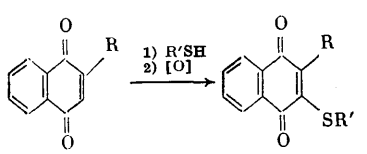
(IX) (X)

By using an excess of thiol, the organothio group may be introduced at various ring positions, depending on the nature of the substituents in the starting quinone. The following trend has been noted: quinones with donor substituents give mainly 2,5-isomers while quinones with acceptor substituents give 2,3-isomers. In such cases, and others, the corresponding 2,6-isomers are also formed. 1,4-Quinones with alkylthio and arylthio groups in the side-chain have attracted the attention of microbiologist and pharmaceutical chemists, as well as organic chemists, since such compounds display high biological activity. In particular, the products of the reaction between 2,3-dimethyl-1,4-benzoquinone and thiophenols are inhibitors of the enzymes succinoxidase and NAD-oxidase. In this respect, compound (XI) (where R = 2-naphthyl) is the most active.[52]



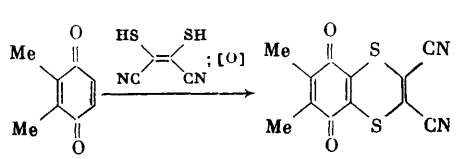
(XI)

Antimicrobial activity has been found with substituted naphthoquinones (XII), prepared as shown below.[53,54]

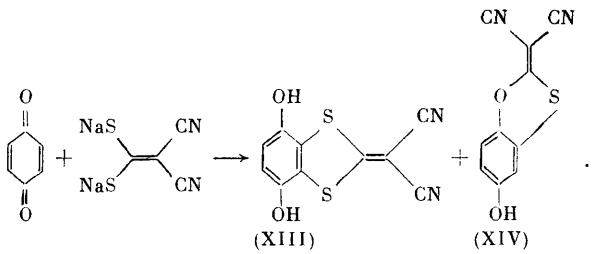


(XII)

While the reactions of thiols with quinones involve two stages (addition and oxidation), the interaction with dithiols involves four steps: (1) addition to the quinone of one mercapto group; (2) oxidation of the intermediate; (3) addition of the other mercapto group; (4) oxidation to give the final product. 2,3-Dimercaptomaleonitrile interacts with 2,3-dimethyl-1,4-benzoquinone according to this scheme with the formation of a rare class of compound, namely 1,4-dithiabenzo-5,8-quinones.[55]

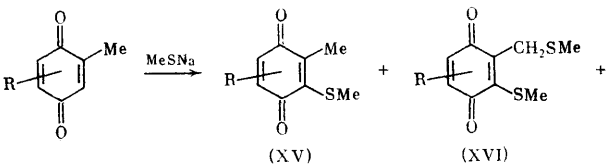


Metal dithiolates react with quinones in a more complex manner to give, in the example below, a mixture of the corresponding benzo-1,3-dithiole (XIII) and benzo-1,3-oxathiole (XIV) in 40% and 20% yield, respectively.[56]

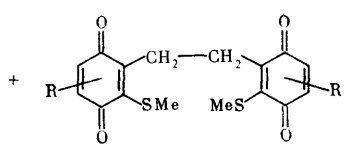


(XIII) (XIV)

Metal thiolates are extremely active nucleophiles, and their reactions with quinones are far more selective than reactions with thiols. The interaction of sodium methylmercaptide with methyl-substituted quinones produces mainly methylthio derivatives (XV)–(XVII) (by addition-oxidation), of which two, (XVI) and (XVII), are substituted in the side-chain.[57,58]

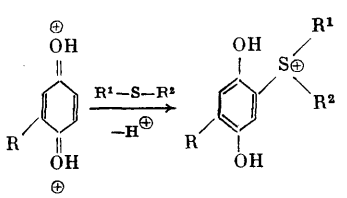


(XV) (XVI)



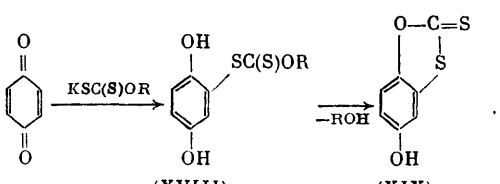
(XVII)

Thioethers on the other hand, are inert towards quinones. However, activation of the latter with 50% H_2SO_4 leads to the formation of sulfoniohydroquinones.[45,59]



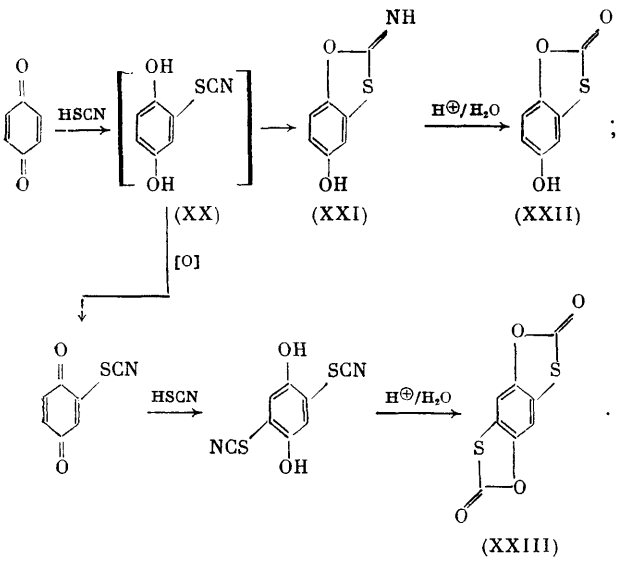
(b) With thiolic acids

In this section, we examine the reactions of quinones with SH-acids containing divalent sulphur. 1,4-Quinones interact with dithiocarboxylic acids and their salts. Reaction with potassium xanthate affords the condensation product (XIX) via the 1,4-adduct (XVIII).[45]



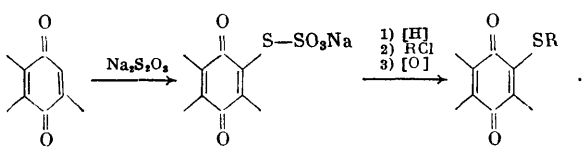
(XVIII) (XIX)

The interaction of thiocyanic acid with 1,4-benzoquinone gives the 1,3-benzoxathiolones (XXII) and (XXIII) rather than the thiocyanatohydroquinone (XX), as might have been expected. The reaction conditions determine which of the products (XXI–XXIII) are isolated.[60]



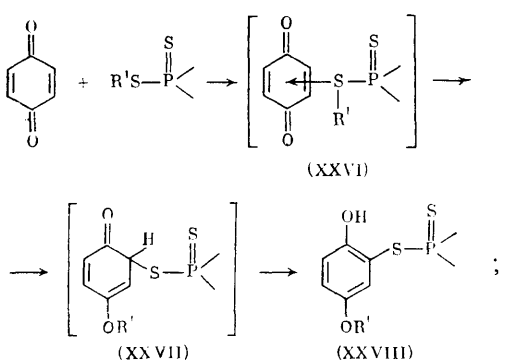
(XX) (XXI) (XXII) (XXIII)

Since the thiolic sulphur of the thiosulphate ion is the nucleophilic centre, the reaction of sodium thiosulphate with quinones leads to the formation of sulfothiohydroquinones (XXIV), which in certain cases have been used for the synthesis of alkylthio-1,4-benzoquinones (XXV).[45]



(XXIV) (XXV)

The interaction of dithiophosphoric acids and their trimethylsilyl esters with quinones is interesting. A detailed study of the reactions by kinetic and spectrophotometric methods has shown that a *p*,π-type complex (XXVI) is formed initially; this leads to intermediate (XXVII), and then to the final 1,4-adduct (XXVIII).

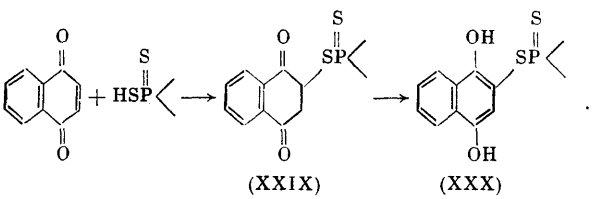


(XXVI)

(XXVII) (XXVIII)

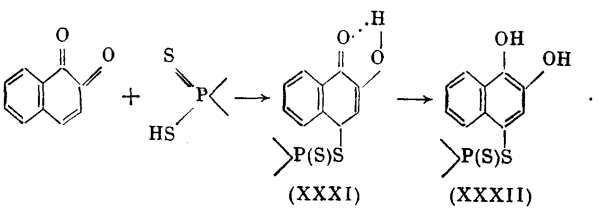
R' = H, SiMe .

The interaction with 1,4-naphthoquinone takes place by another route.



(XXIX) (XXX)

Initially, addition takes place across the C=C bond of the quinone to give (XXIX), which is converted into the thiophosphorylated dihydroxynaphthalene (XXX). The reaction of dithiophosphorus acids with 1,2-naphthoquinone is unusual. The intermediate (XXXI), which can be detected by IR-spectroscopy, isomerises as reaction progresses to give the 1,4-adduct (XXXII) as the final product.

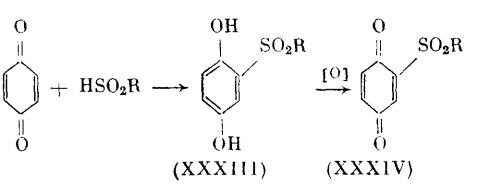


(XXXI) (XXXII)

The stability of the enol form of intermediate (XXXI) is energetically favourable by virtue of stabilisation by intramolecular hydrogen bonding.[61–63]

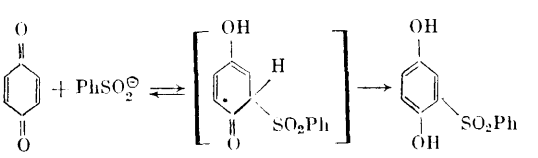
c) With sulphinic acids and sulphurous acid salts

Nucleophilic addition of sulphinic acids to 1,4-benzoquinone proceeds smoothly in the absence of catalyst to give the corresponding 2,5-hydroxy-1-alkyl(or aryl)sulphonylbenzenes (XXXIII), which can be converted to the corresponding sulphonylquinones (XXXIV).



(XXXIII) (XXXIV)

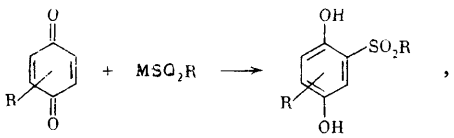
The mechanism of the reaction between 1,4-benzoquinone and phenylsulphinic acid in an aqueous medium has been established by kinetic studies with isotopes. Initially, there is a reversible addition of sulphinate anion to the ring system of the quinone to give an unstable adduct, which then isomerises to the sulphonylhydroquinone (XXXIII) as final product.



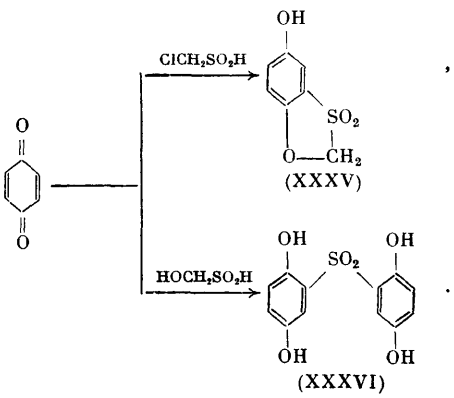
(XXXIII)

Kinetic data are in accord with a second order process, being first order in each reactant. The limiting step of the reaction is dependent on the pH of the medium. Thus, below 3.1, the rate-limiting step is the initial addition, while above pH 4.0 the isomerisation is the rate-determining stage.[64]

Sulphinic acid salts are stronger nucleophiles than the parent acids. They react with quinones to give sulphonylhydroquinones:[65]



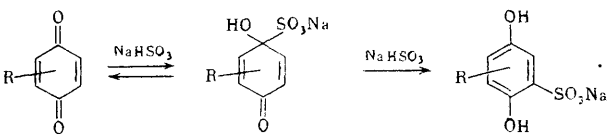
where M is an alkali or alkaline-earth metal or an organic cation. Chloromethanesulphinic and hydroxymethanesulphinic acid, as well as other sulphinyl compounds, interact with 1,4-benzoquinone to give unstable 1,4-adducts, which undergo intra- and inter-molecular condensation with the formation of the corresponding sulphones (XXXV) and (XXXVI).[45]



(XXXV)

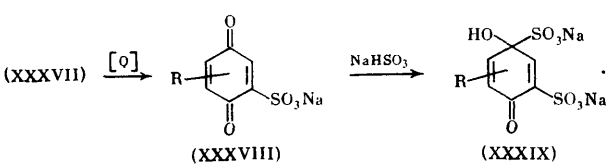
(XXXVI)

Reaction of sodium bisulphite with 1,4-benzoquinones involves a rapid, reversible, formation of a carbonyl-bisulphite adduct, followed by addition of bisulphite anion to give the hydroquinone-monosulphonates (XXXVII) as final product.[66,67]



(XXXVII)

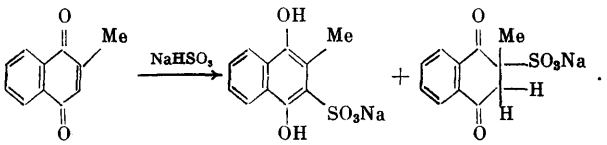
A study of this reaction in buffered medium at pH 5–10 has shown that the highly reducing species (XXXIX) is formed. Its redox potential is more negative than that of hydroquinone. Thus, it is reasonable to conclude that compound (XXXIX) plays an important role in the mechanism of the action of hydroquinone-type indicators. It has been shown that compound (XXXIX) is formed by oxidation of the monosulphonate (XXXVII), followed by addition of sodium bisulphite to the carbonyl group of (XXXVIII).[68]



(XXXVIII)

(XXXIX)

In the reaction of sodium bisulphite with 2-methyl-1,4-naphthoquinone a 1,2-adduct (XLI) is formed as well as the expected 1,4-adduct (XL). This 1,2-adduct arises by an unusual nucleophilic addition to the carbon-carbon double bond of the quinone.[68]

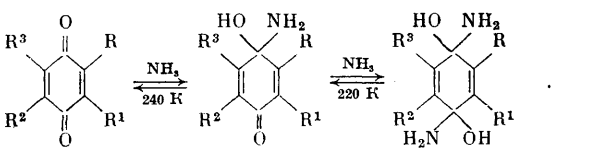


(XL)

(XLI)

3. Reactions with *N*-nucleophiles

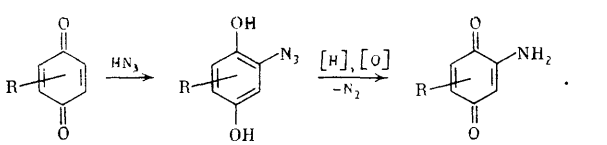
Gaseous ammonia interacts with unsubstituted quinones to give unstable amorphous products. Liquid ammonia reacts with substituted 1,4-benzoquinones at 240 K to give 1:1 adducts (XLII). At 220 K the diadduct (XLIII) is formed. The reaction is reversible: by addition of methylene chloride, followed by removal of ammonia, the starting 1,4-benzoquinones may be recovered.[69]



(XLII)

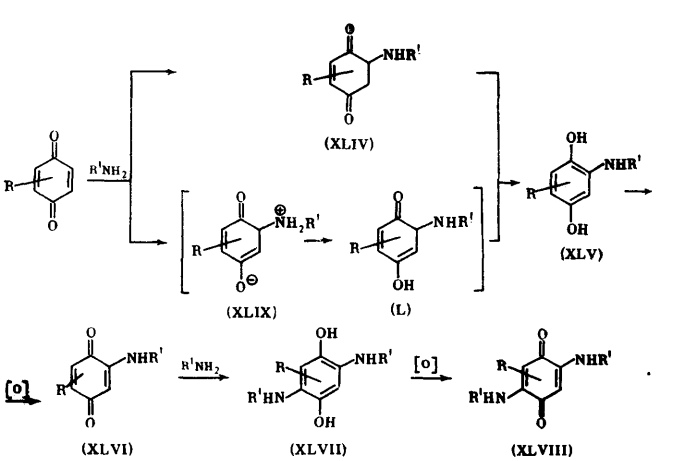
(XLIII)

Nucleophilic addition of hydrazoic acid to 1,4-quinones provides a key method of preparing azidoquinones, from which aminoquinones can be obtained.[45,64]



a) With primary amines

1,4-Benzoquinones react with primary aliphatic amines to give 2,5-diamino-1,4-benzoquinones (XLVIII), which are formed via oxidation of the intermediate 2,5-diaminohydroquinones (XLVII). It was not possible to isolate the initially-formed mono-aminated derivatives, (XLIV) and (XLVI).[70] This is possibly the reason why 2-amino-1,4-benzoquinones have not been reported.



(XLIV)

(XLV)

(XLIX)

(L)

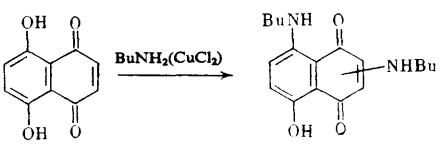
(XLVI)

(XLVII)

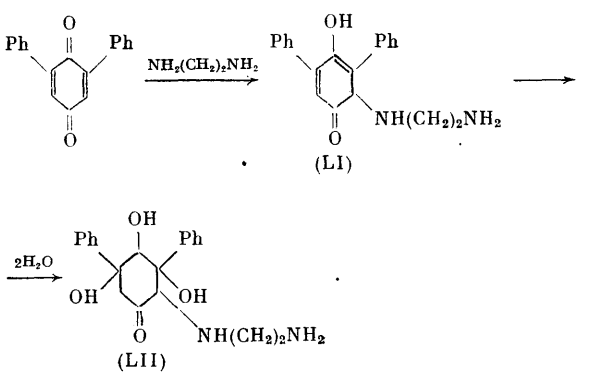
(XLVIII)

As shown above, the mechanism of the reaction involves an initial addition of the amine across a carbon-carbon double bond to give intermediate (XLIV), which isomerises into the aminohydroquinone (XLV) followed by oxidation to the monoaminoquinone (XLVI). Addition of a second amine molecule then gives the diaminoquinone (XLVIII).[45] In our opinion, reaction involves initial formation of a bipolar intermediate (XLIX), which isomerises into the cyclohexadienone (L) and thence to the aminohydroquinone (XLV). Such a scheme accords with the generally accepted mechanism of nucleophilic addition to unsaturated carbonyl compounds.[71]

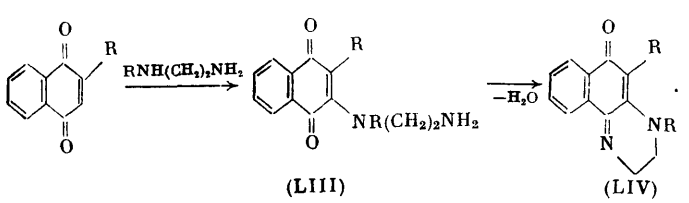
The interaction of 1,4-naphthoquinones with aliphatic amines leads to the formation of 2-amino-1,4-naphthoquinones. If there is a hydroxy substituent in the 1,4-naphthoquinone, then substitution takes place as well as addition-oxidation. 5,8-Dihydroxy-1,4-naphthoquinone reacts with butylamine in the presence of $CuCl_2$ to give 2,8- or 3,8-bis(butylamino)-5-hydroxy-1,4-naphthoquinone as the main product. The yield is less in the absence of catalyst.[72]



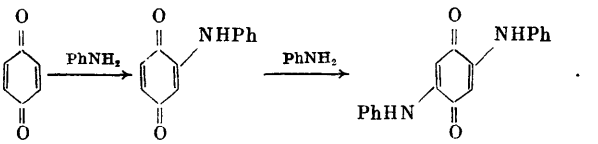
Reactions of 1,4-quinones with aliphatic diamines leads to the formation of a more complex product. The interaction of 2,6-diphenyl-1,4-benzoquinone with 1,2-diaminoethane, for example, affords an intermediate cyclohexadienone (LI), to which two water molecules add to give the cyclohexanone (LII) as final product. 1,6-Diaminohexane and piperazine react similarly.[73]



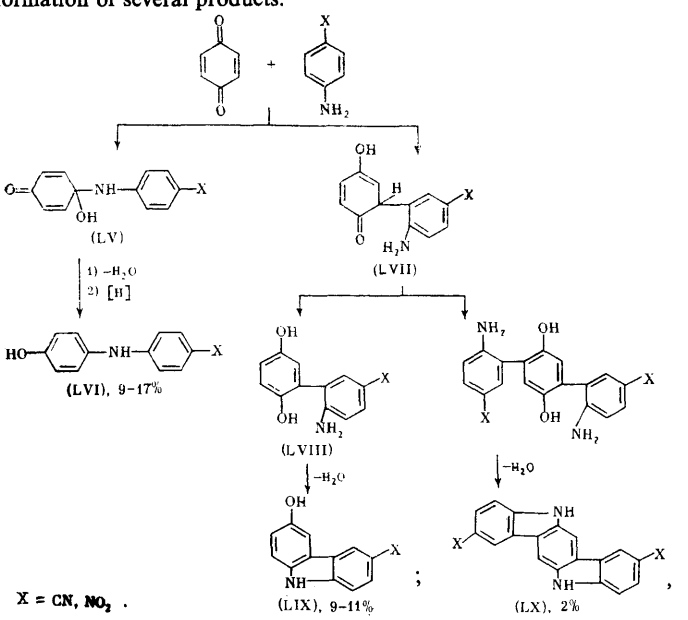
1,4-Naphthoquinone with diamines provides an initial 1,4-adduct (LIII), which subsequently loses a molecule of water to give a cyclic quinone imine (LIV).[74]



Aromatic amines are less active than aliphatic amines in their nucleophilic addition to quinones. As aniline is relatively inert, it has been possible to isolate both 2,5-dianilino-1,4-benzoquinone and 2-anilino-1,4-benzoquinone.[45]

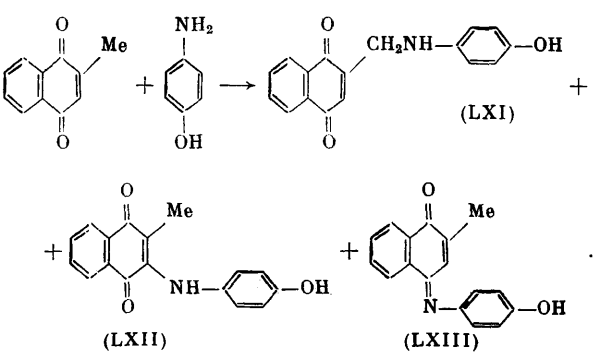


In a study of the interaction of substituted anilines with quinones (Nenitzescu reaction), low selectivity was recorded with the formation of several products.[75]

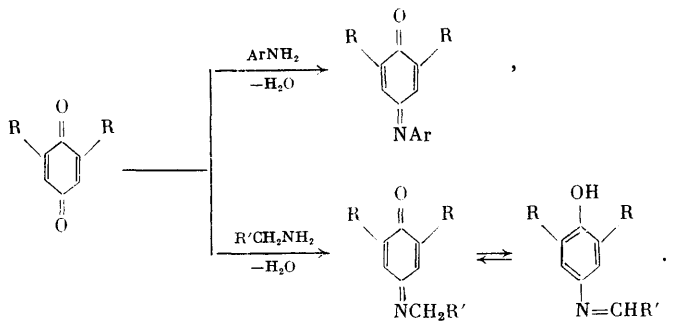


A reaction scheme was proposed according to which the final products (LVI, LIX, LX) were formed in parallel sequences: 1) 1,2-addition of aniline to a carbonyl group of the quinone to give the quinone aminoacetal (LV), followed by dehydration and reduction to produce the diphenylamine (LVI); 2) 1,4-addition of aniline to the conjugated system of the quinone to give the intermediate cyclohexadienone (LVII), which aromatises to the substituted hydroquinone (LVIII); the latter then dehydrates to give the carbazole (LIX). A second molecule of the starting aniline may also add to the cyclohexadienone, ultimately providing the dicarbazole (LX).

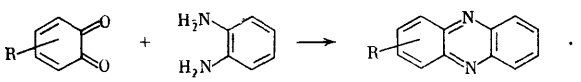
Several products are formed by interaction of 2-methyl-1,4-naphthoquinone with *p*-aminophenol. Thus, radical substitution affords quinone (LXI), while nucleophilic addition gives quinone (LXII) and quinone imine (LXIII).[76,77]



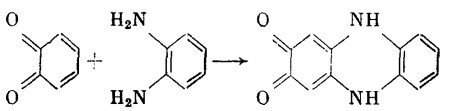
2,6-Disubstituted 1,4-benzoquinones, in which 1,4-addition is prevented by steric and electronic factors, react with primary aromatic amines by a condensation mechanism.[45,78]



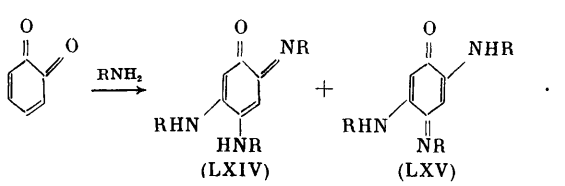
1,2-Quinones react vigorously with both aliphatic and aromatic amines in the same way as 1,4-quinones. However, it is possible to distinguish between 1,2- and 1,4-quinones by treatment with *o*-phenylenediamine: 1,2-quinones afford phenazine derivatives, whereas 1,4-quinones are unreactive



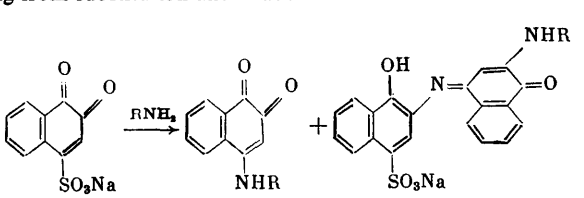
In the case of 1,2-benzoquinone itself, such a condensation does not take place; instead, an addition-oxidation leads to the formation of another type of cycloadduct.[45,64]



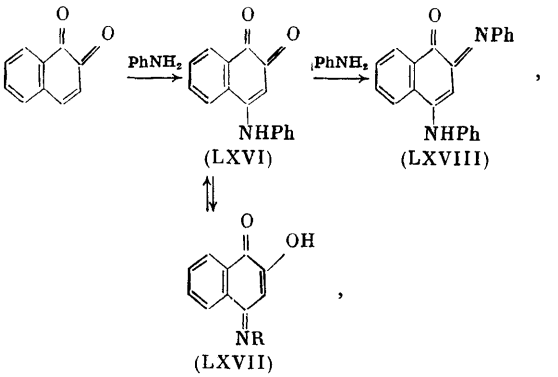
In general, unsubstituted 1,2-quinones react with amines by 1,4-addition. In the case of aromatic amines reaction is selective, but with aliphatic amines reaction is complicated by a concurrent condensation. For example, treatment of 1,2-benzoquinone with methyl-, ethyl-, propyl- and butyl-amine gives two types of product: 1,2-quinone imines (LXIV) and 1,4-quinone imines (LXV), formed as a result of consecutive double addition-oxidation and condensation.[79]



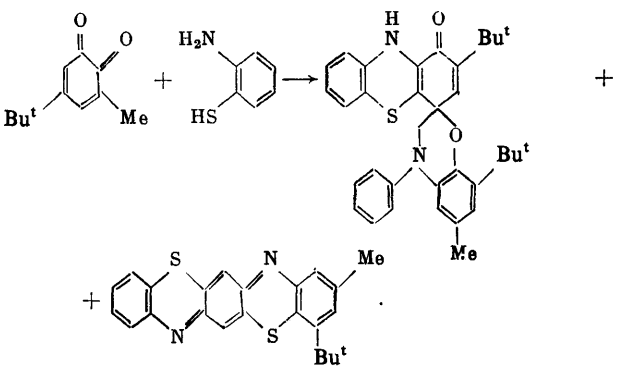
1,2-Naphthoquinone and substituted derivatives react with primary aliphatic amines to give several products, the most important resulting from substitution and condensation.[80]



Aniline participates in 1,4-addition with 1,2-naphthquinone, affording, after air oxidation, 4-anilino-1,2-naphthoquinone (LXVI) as the only isolable product.



If the reaction is carried out in the liquid phase, a second aniline molecule is added to give the quinone imine (LXVIII) as the final product.[45] It has been established that the substituted 1,2-quinone (LXVI) exists in the quinoidal form in the solid state or in alcoholic media, whereas it exists in the 1,4-quinone imine form (LXVII) in trifluoroacetic acid.[81] The reaction of 1,2-quinones with amines can be applied successfully for the preparation of complex structures which may be difficult or impossible to prepare by other means. The condensation of equimolar amounts of *o*-aminothiophenol and substituted 1,2-benzoquinones in the presence of $FeCl_3$ leads to the formation of unusual phenothiazines.[82]

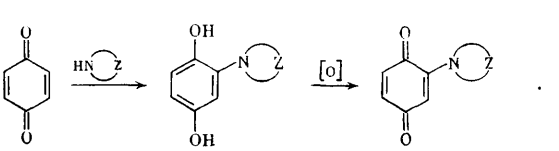


Quinone oximes with a variety of substituents are obtained by reaction of 4-substituted 1,2-naphthoquinones with ethylenediamine.[83]

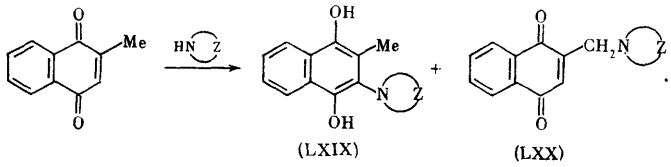
4,4'-Bis(1,2-naphthoquinone) interacts with aromatic amines in the same way as other 4-substituted 1,2-naphthoquinones to give condensation products involving the carbonyl group at the 2-position.[84,85]

b) With secondary amines

Secondary C_1-C_4 amines yield monoamino-substituted 1,4-benzoquinones exclusively.[64] Treatment of 1,4-benzoquinones with heterocyclic amines affords 2-substituted hydroquinones which are oxidised in air to give the corresponding quinones.[86]

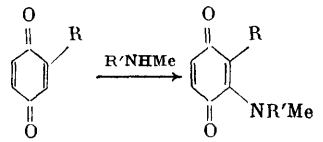


2-Methyl-1,4-naphthoquinones with pyrrolidine, piperidine, and heptamethyleneimine give stable 1,4-adducts (LXIX) as well as products derived by substitution of hydrogen at the methyl group (LXX).[87]



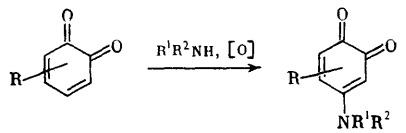
(LXIX) (LXX)

The study of the reaction of quinones with secondary amines has led to the development of the chemistry of biologically active quinones. Thus, aminoquinones (LXXI) have been prepared by interaction of 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-methyl-1,4-naphthoquinone and other 1,4-quinones with the following psychopharmacologically active amines: desipramine, nortryptyline, protryptyline, maprotyline and benzooctamine.[88–91]



(LXXI)

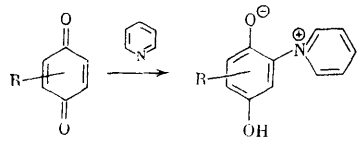
Treatment of 1,2-quinones with secondary amines affords 1,4-adducts which are converted to 4-amino,1,2-benzo(naphtho)-quinones in air.[45]



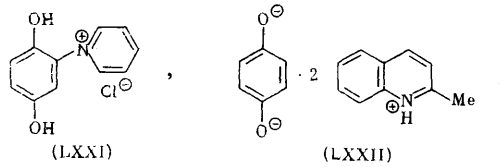
c) With tertiary amines and pyridine

In contrast with primary and secondary amines, tertiary amines do not react with quinones by nucleophilic addition. However, they do react with quinones by forming 1:1 or 1:2 charge-transfer complexes. In certain cases, complexes have been isolated and characterised as distinct entities,[92] but mostly they have only been detected by spectroscopic methods. The absorption of the complexes accords with a $p-\pi^*$-type transfer from the HOMO of the donor (amine) to the LUMO of the acceptor (quinone). The stability of the complexes depends markedly on the donor-acceptor properties of quinone-amine pair.[93]

The reaction of quinones with pyridine which, like tertiary amines lacks a labile hydrogen, is interesting in that there is no distinct complex-forming stage. Reaction proceeds directly to a bipolar compound.



2-Pyridiniohydroquinone chloride (LXXI) is obtained in the presence of HCl. A similar adduct is formed by reaction of quinones with quinoline. The salt (LXXII) is isolated from the interaction with quinaldine.[45]



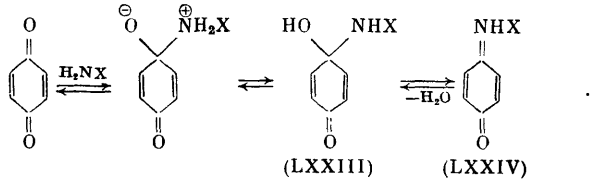
(LXXI) (LXXII)

Charge-transfer complexes are not only formed with tertiary amines. Others participate in the same way, e.g. aniline, toluidine, ethylamine, diethylamine, piperidine, and polyvinylpyridine.[94–96]

Thus, in the overall scheme for nucleophilic addition of amines to quinones, as illustrated above, there could be an additional stage involving the formation of a charge-transfer complex. However, it is clear that certain reactions of amines with quinones do not involve complex formation.

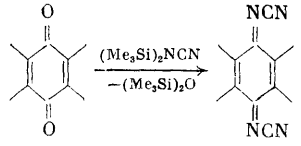
d) With cyanamide, hydroxylamine, hydrazines and hydrazides

This section is devoted to the reaction of quinones with *N*-nuclophiles, H_2NX, where X = CN, OH, NRR', NHC(O)R and $NHP(O)R_2$. Here, reaction takes place at a carbonyl function rather than by addition to the conjugated double bond (C=C–C=O). The mechanism of the reaction involves several reversible steps, of which the most important are nucleophilic addition of the nitrogen atom to the carbonyl group with formation of quinol (LXXIII), and dehydration of the latter with formation of quinone imine (LXXIV).

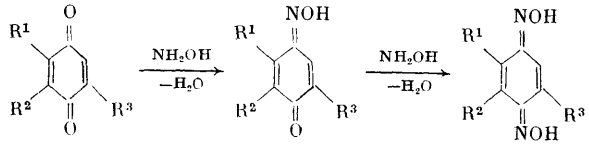


(LXXIII) (LXXIV)

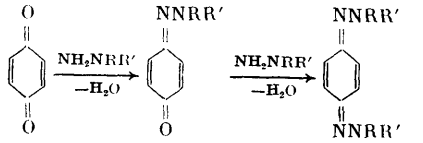
Quinones do not react with cyanamide. However, they react with silylcyanamides.[97]



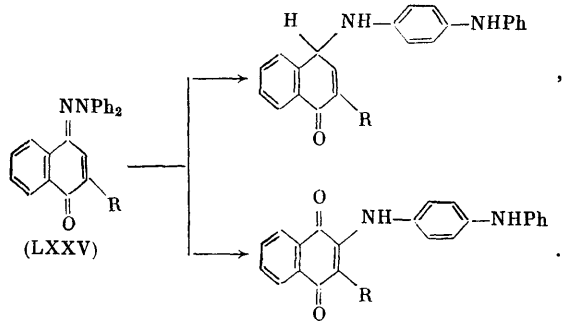
Hydroxylamine converts quinones into quinone mono- and di-oximes, which are particularly interesting as precursors for the synthesis of certain aromatic dinitroso compounds. More details on the oximation of quinones can be found in a monograph.[98]



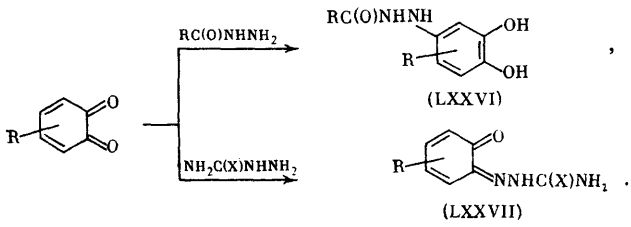
Hydrazine derivatives react with 1,4-quinones to give the corresponding quinone mono- and di-hydrazones.[99]



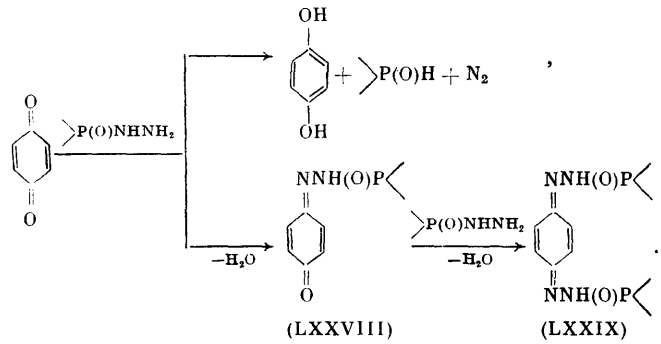
A redox reaction has been noted in certain cases, notably in the reaction with phenylhydrazine.[100–103] In this respect, we have focussed on the reaction of 1,4-naphthoquinones with diphenylhydrazine. Depending on the nature of the ring substituent, the initial condensation product (LXXV) is either converted to a semidine derivative or undergoes prototropic rearrangement.[104,105]



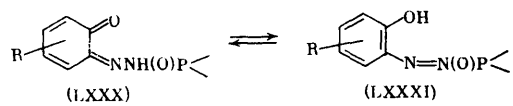
However, the nature of the hydrazine derivative, itself, largely determines the outcome of the reaction of 1,2-quinones. Thus, treatment of 1,2-quinones with hydrazine affords pyrocatechols by reduction. Acylhydrazines convert 1,2-quinones into 1,2-dihydroxy-3-acylhydrazinobenzenes (LXXVI), while semicarbazides and thiosemicarbazides condense to give the corresponding quinone semicarbazones (LXXVII).[45]



Phosphorohydrazidates react with quinones in a rather peculiar manner. Under mild conditions condensation takes place with the formation of phosphorylated quinone hydrazones (LXXVIII) and (LXXIX); however, above 20 °C in polar solvents, a redox reaction is set up, leading to hydroquinone, the corresponding phosphorus(III) acid, and nitrogen.[106–108]



Monohydrazones (LXXX) are formed with 1,2-quinones. There was no dihydrazone formation, probably because of steric hindrance.

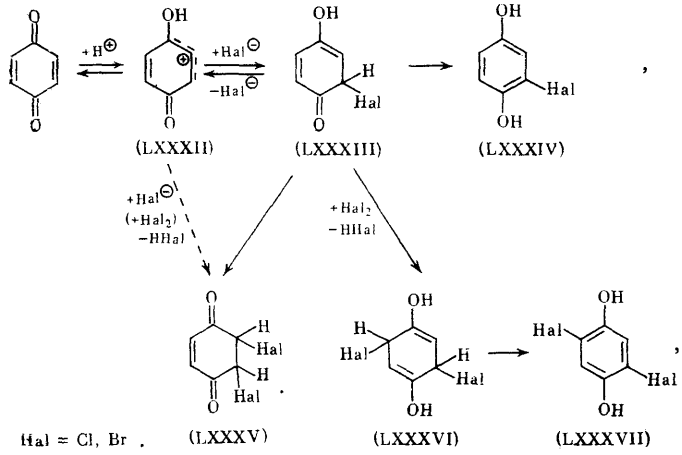


It has been established that the position of the quinone hydrazone ⇌ azophenol (LXXXI) equilibrium is largely determined by the nucleophilicity of the medium and the nature of the substituent on the quinoidal ring.[109]

Quinone hydrazones have been scrutinised for their biological activity. Notably, 1,4-naphthoquinone 4-aryl(aroyl)hydrazones have been prepared and shown to possess antimicrobial activity; they are potential tuberculostatic agents.[110]

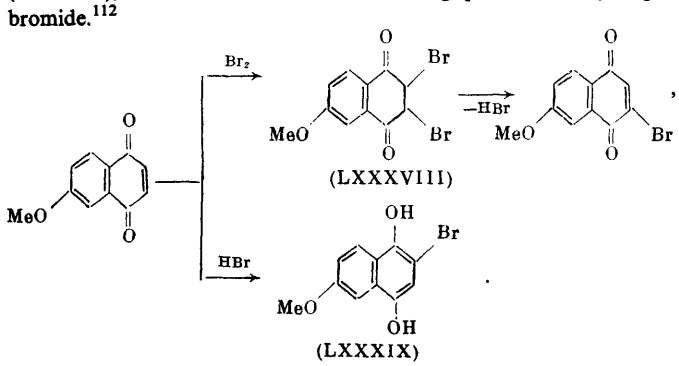
4. Reactions with halogen nucleophiles

Hydrogen iodide does not add to quinones, but reduces them to hydroquinones. Other hydrogen halides participate in 1,4-addition to give halogenohydroquinones (LXXXIV).[45,64,111]

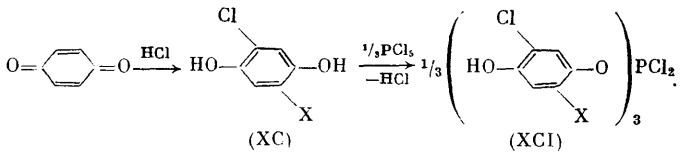


Reaction is initiated by protonation of the quinone with formation of cation (LXXXII); this undergoes attack by halide ion to give the corresponding 1,4-adduct (LXXXIII), which subsequently isomerises to the corresponding halogenohydroquinone (LXXXIV) as the final product. If free halogen is present in the medium, then adduct (LXXXIII), which by virtue of its unusual structural features is a very active nucleophile, adds a further halogen atom to give the dihalogenoquinone (LXXXV) or the cyclohexadiene (LXXXVI), stabilised in the dihalogenohydroquinone form (LXXXVII). It has been noted that the route (LXXXII → LXXXIII → LXXXIV) is more favourable than the route (LXXXII → LXXXIII → LXXXVI → LXXXVII) for steric reasons.[111]

In this section, it has also been considered appropriate to examine reactions of quinones with electrophilic reagents where the key step in the process involves nucleophilic addition. For example, the interaction of 6-methoxy-1,4-naphthoquinone with bromine affords, in addition to adduct (LXXXVIII), the nucleophilic addition product (LXXXIX), which is formed from the starting quinone and hydrogen bromide.[112]



The reaction of PCl_5 with 1,4-benzoquinones proceeds in a similar way.



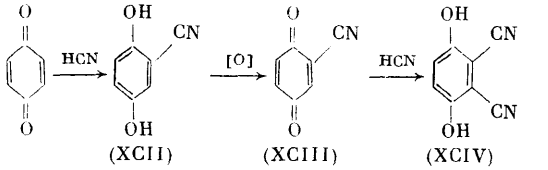
(XC) (XCI)

The interaction involves an autocatalytic chain process, the initial stage being the addition of hydrogen chloride to the quinone. The resulting chlorohydroquinone (XC) condenses with PCl_5 to give the dichlorophosphorane (XCI) as the final product with elimination of hydrogen chloride. The latter then adds to the starting quinone, thereby perpetuating the chain reaction.[113,114]

5. Reactions with *C*-nucleophiles

(a) With CH-acidic compounds

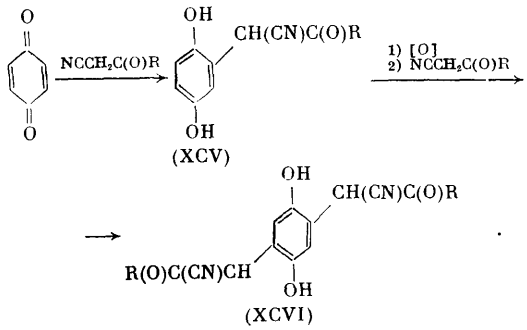
Hydrogen cyanide adds to 1,4-benzoquinone to give adduct (XCII), which is oxidised to the cyanoquinone (XCIII).



(XCII) (XCIII) (XCIV)

The interaction of a second HCN molecule with the cyanoquinone (XCIII) proceeds in an anomalous manner. Usually, all reactions of mono-substituted 1,4-quinones involve addition of nucleophiles at the 5-position (i.e. the *para*-position relative to the substituent). However, in the above case, the cyano group enters at the 3-position of the quinone to give (XCIV). There is no convincing explanation of this anomaly in the literature. Nevertheless, this reaction is preparatively very important for the synthesis of a number of cyanoquinones, amongst which the oxidant, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.[115]

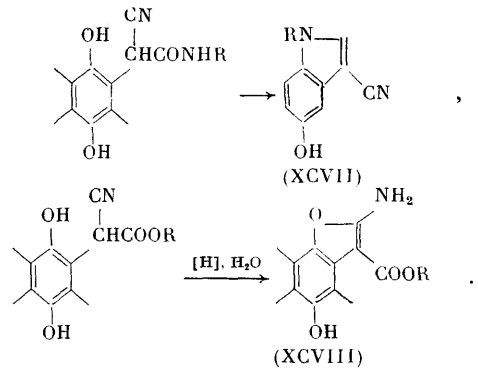
Of CH-acidic compounds, those with active methylene groups have been most studied in connection with quinone substitution. Carbonyl and nitrile substituents normally serve as activators.



(XCV) (XCVI)

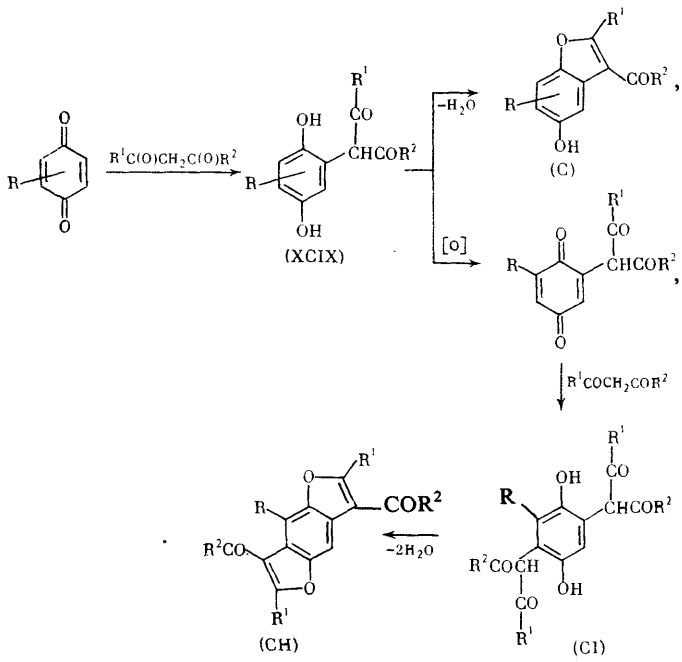
Thus, interaction of 1,4-quinones with 3-oxocarbonitriles involves initial 1,4-addition, followed by isomerisation of the resulting adduct to give the alkylhydroquinone (XCV). Oxidation of the latter, followed by addition of a second molecule of the nucleophile, may lead to the corresponding 2,5-dialkylhydroquinone (XCVI).[45,116,117]

Certain products undergo intramolecular cyclisation to give indoles (XCVII) and furans (XCVIII).[117,118]



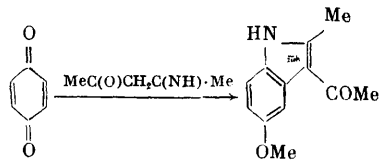
(XCVII) (XCVIII)

1,3-Dicarbonyl compounds and their derivatives react with quinones in a similar manner. The initially-formed 1,4-adduct (XCIX) is subsequently converted to benzofuran (C) via cyclodehydration, or undergoes oxidation-addition [to adduct (CI)] followed by cyclodehydration to the difuran (CII).[119,120]

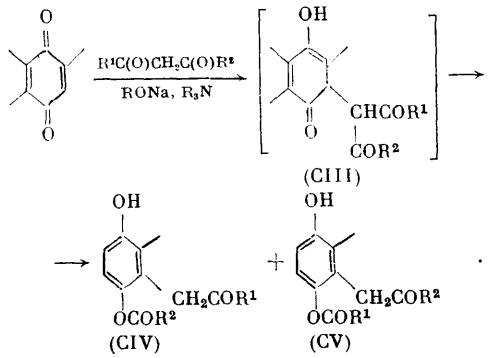


(XCIX) (C) (CH) (CI)

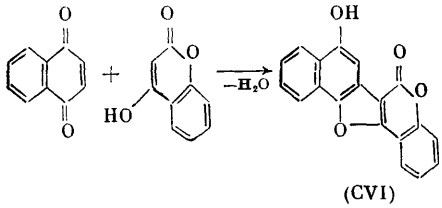
In certain cases, other processes are involved. Thus, the interaction of 1,4-benzoquinone with acetylacetone imine affords, unexpectedly, an indole derivative with a methoxy substituent in the benzene ring.[121]



In the presence of strong base, the reaction of substituted 1,4-benzoquinones with 1,3-diketones proceeds with the formation of substituted phenols (CIV) and (CV), rather than an adduct of type (XCIX). This is associated with an acylotropic conversion of intermediate (CIII).[122–125]

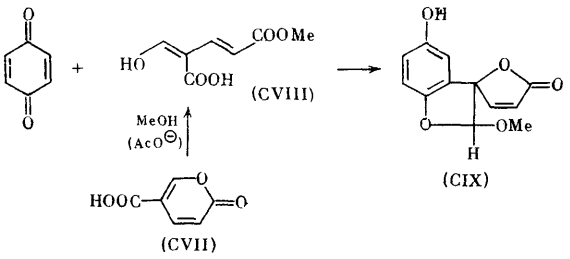


The reaction with 4-hydroxycoumarin is worthy of consideration here since, although it is not formally a CH-acidic compound, it can be viewed as the tautomeric form of a 1,3-dicarbonyl compound. Treatment with 1,4-naphthoquinone affords an adduct which subsequently cyclodehydrates to give furan (CVI).[126]



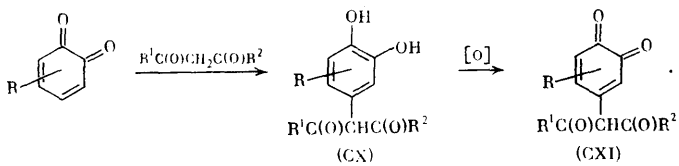
(CVI)

The spirobutenolide (CIX) is obtained by reaction of 1,4-benzoquinone with coumalic acid (CVII) in the presence of methanol, sodium acetate and acetic acid.



It is thought that acetate ion initiates pyrone ring opening with formation of enol (CVIII), which serves as a reactive form of coumalic acid.[127]

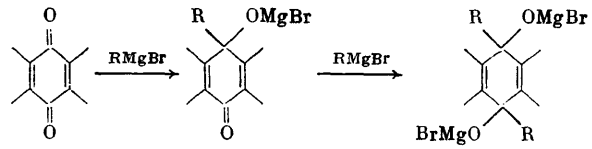
1,2-Quinones react with CH-acidic compounds in the same manner as 1,4-quinones to yield adducts (CX).[128–130]



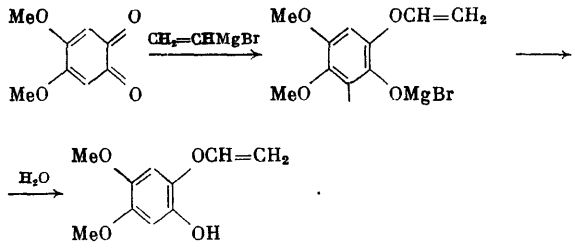
However, contrasting with the 1,4-quinone adducts (XCIX), which undergo a variety of reactions, the adducts (CX) are only oxidised with the formation of the corresponding 1,2-quinones (CXI).

b) With organometallic compounds

Substituted quinones react with the strongly nucleophilic Grigard reagents by nucleophilic addition. Addition to *p*-quinones involves one or both carbonyl groups.[45]

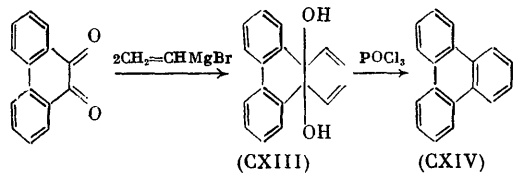


The reaction of vinylmagnesium bromide with 4,5-dimethoxy-1,2-benzoquinone leads to an adduct which is hydrolysed to a pyrocatechol vinyl ether (CXII).[131]

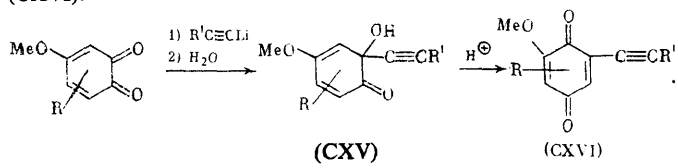


CXII

The interaction of vinylmagnesium bromide with phenanthraquinone yields the divinyldiol (CXIII) which is converted to triphenylene (CXIV) on treatment with $POCl_3$. Polycyclic hydrocarbons can thus be prepared by this route.[132]



Lithium acetylide adds to a carbonyl group of 1,2-benzoquinones with the formation of cyclohexadienones (CXV). In acidic media, the latter is hydrolysed to the relatively inaccessible alkynylquinones (CXVI).[133,134]



In this way, highly active nucleophiles, such as organometallic compounds, may add to one of the carbonyl groups of a quinone if the other is sterically hindered.

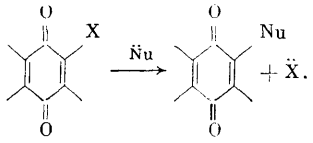
6. Reactions with *P*-nucleophiles

A vast amount of data is available on the interaction of organometallic compounds with quinones. In the majority of cases, the central atom of the organoelemental compound is not the reactive centre. Other reports deal with nucleophilic processes where

a heteroatom (in most cases phosphorus or arsenic) serves as the nucleophilic centre. In organophosphorus chemistry, it has been shown that almost all derivatives of di-, tri- and tetra-coordinated phosphorus acids, where the phosphorus atom is the reactive centre, interact with quinones via nucleophilic addition. A variety of products are obtainable depending on a number of factors, the most important being the nature of the substituents in the organophosphorus compound. More detailed information on the reactions of organophosphorus compounds with quinones are given in an earlier review.[135]

III. Nucleophilic substitution of quinones

The reactivity of quinones towards nucleophiles is dependent to a large degree on the π-acceptor character of the quinones. The π-acceptor properties are dependent primarily on the energy and symmetry of the lower unfilled molecular orbital (LUMO). In its turn, the energy of the latter is a function of electron affinity. Complex formation is one way to enhance electron affinity.[136–149] For example, in the complexes between 1,4-benzoquinone and $GaCl_3$ or $AlCl_3$, the structure of the LUMO is not changed, but its energy decreases from 0.15 to −1.7 eV.[145] This leads to an increased reactivity of the complexed quinone towards nucleophiles. Although quinone complexes with proton,[45] Lewis acids[137,141,142] and metal ions[139,140,147] have been used preparatively, the full potential of such quinone activation towards nucleophiles has not yet been explored. Electron affinity can also be increased by appropriate substitution of the quinone. Thus, the electron affinity of unsubstituted 1,4-benzoquinone is relatively low (1.91 eV),[146] but replacement of hydrogen by other atoms leads to a shift in electron affinity. Alkyl substitution, for example, lowers the value (1.59 eV for duroquinone), while halogens and, in particular, the cyano group, effect a marked increase (2.78 eV for chloranil, 2.50 eV for bromanil, and 3.40 eV for tetracyano-1,4-benzoquinone).[64,146] Thus, halogeno- and pseudohalogeno-quinones are the most reactive of substituted quinones towards nucleophiles.

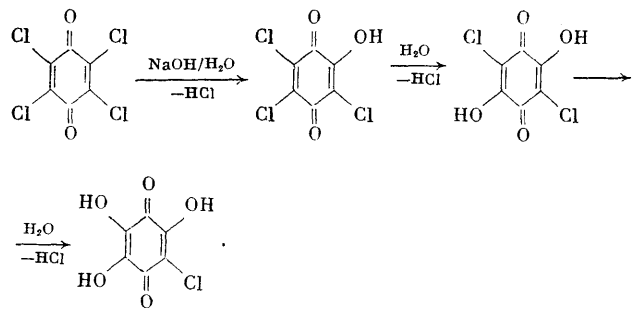


Both anions and neutral compounds with a free lone pair may be used as nucleophiles. The quinone may be substituted by halogen or a pseudohalogen or, in fact, any other electron-accepting group where polarisation of the C−X bond is possible.

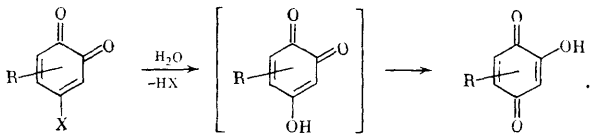
1. Reactions with *O*- and *S*-nucleophiles

The hydrolysis of halogenoquinones to hydroxyquinones is a classical example of a nucleophilic substitution of a quinone. Replacement of the halogen by a hydroxyl group proceeds most simply in the presence of a base—alkaline or pyridine. Acid-catalysed hydrolysis is rare. The completion of the reaction depends to a large extent on the effect of the ring substituent. Nevertheless, catalytic hydrolysis of substituted quinones normally proceeds readily and selectively in high yield.

With chloranil, exchange of chlorine atom by a hydroxyl group takes place in the presence of aqueous NaOH. Mono- and di-substituted hydroxyquinones can be prepared as required.

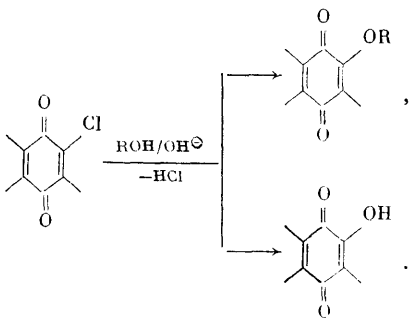


Hydrolysis of bromanil and fluoranil proceeds in the same way. With iodanil replacement of only one halogen atom is possible.[150] Quinones with alkoxy-, aryloxy-, alkylthio-, or arylthio-groups participate in a catalytic reaction with water. In each case, replacement of the substituents by a hydroxyl group takes place. However, substituted 1,2-quinones hydrolyse by a different route. The initially formed hydroxy-1,2-quinones (CXVII) are spontaneously converted into the energetically more favourable hydroxy-1,4-quinones (CXVIII).[45]

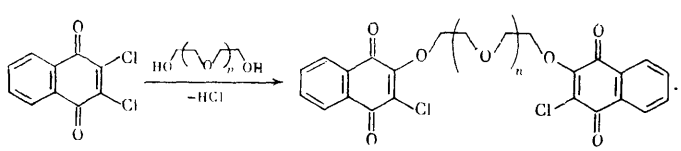


(CXVII) (CXVIII)

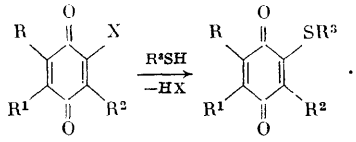
The interaction of halogenoquinones with alcohols and phenols normally proceeds in the presence of a base as catalyst, principally alkali metal alkoxides and aroxides or NaOH. As a rule, alkyoxylation or aryloxylation of the quinones takes place, although hydrolysis to hydroxyquinones has sometimes been observed.[151–153]



The alcoholysis of 2,3-dichloro-1,4-naphthoquinone was studied as long ago as the last century, and nowadays has found practical applications, notably in the synthesis of crown ethers with naphthoquinone fragments.[152,153]



The interaction of substituted quinones with aliphatic mercaptans and thiophenols is important since it permits the preparation of quinones with a sulphur functionality at a defined position.

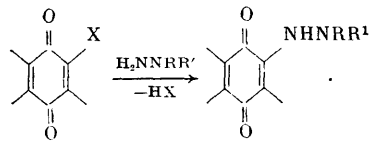


A base is required for the reaction of quinones with aliphatic mercaptans, and references have been made to the use of catalysts for the reaction with thiophenols.[45,64,154]

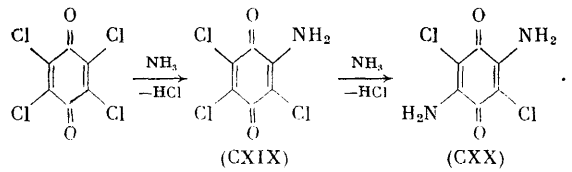
2. Reactions with *N*-nucleophiles

Nucleophilic substitution of quinones has been studied mostly with amines and other *N*-nucleophiles. The reactivity of *N*-nucleophiles decreases in the order: hydrazines ≥ ammonia > primary amines > secondary amines. The reactivity of aromatic amines is lowered by bulky substituents. Electron-accepting substituents in the benzene ring of aromatic amines also inhibits the reaction.

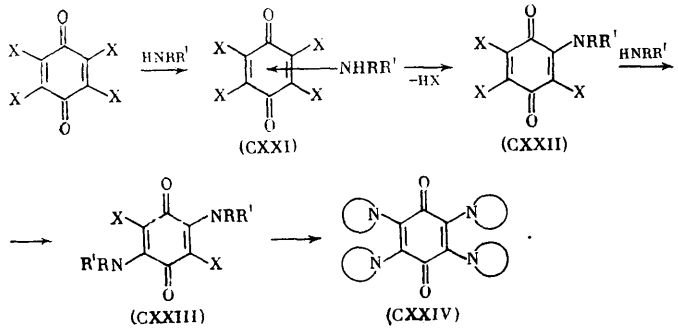
Hydrazines react with 1,4-quinones to give hydrazinoquinones.[155–157]



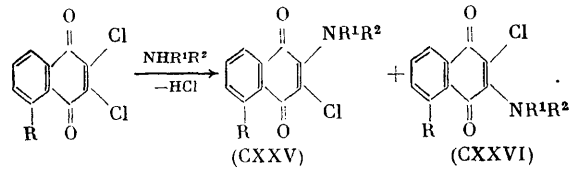
Treatment of chloranil with ammonia initially affords a monoaminoquinone (CXIX), which is further aminated to the diaminoquinone (CXX). The structure of the latter has been established by X-ray spectroscopy.[158]



The mechanism of the reaction of halogenanils with amines with a single N–H bond involves an initial complex formation to give (CXXI), which is subsequently converted into mono-, di- and tetraaminoquinones (CXXII–CXXIV).[159–164]



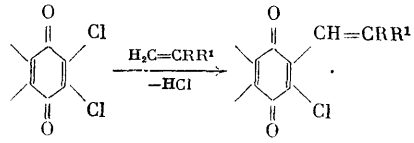
Such replacement of all halogen atoms is only possible with active cyclic amines (pyrazoles, imidazoles, 1,2,3- and 1,2,4-triazoles).[165,166] Treatment of halogen-substituted naphthoquinones with amines affords mono-amino derivatives, (CXXV) and (CXXVI). Both halogen atoms can be replaced by using nitrogen-containing heterocyclics.[167–185]



Studying this reaction has furnished much information: the ratio of 2-chloro- and 3-chloro-isomers (CXXV and CXXVI) is dependent on the structure of the amine;[169–172] this ring substituent influences the reactivity of the amine and the spectral characteristics of the products;[169] optimum conditions have been established for the synthesis of intensely coloured light-sensitive materials;[173] a convenient method of aminating halogenonaphthoquinones by phase transfer catalysis has been found;[174] and water-soluble naphthoquinones have been synthesised.[175,176]

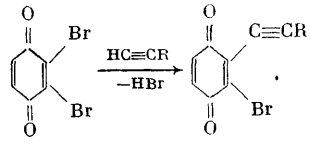
3. Reactions with *C*-nucleophiles

Halogenoquinones condense with *C*-nucleophiles to give quinoidal products with a new carbon–carbon bond. Olefins with an activated double bond interact with chloranil and 2,3-dichloro-1,4-naphthoquinone, providing alkenyl-substituted quinones.[177–180]

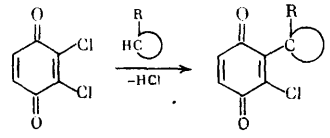


R = R¹ = OAlk, NAlk₂

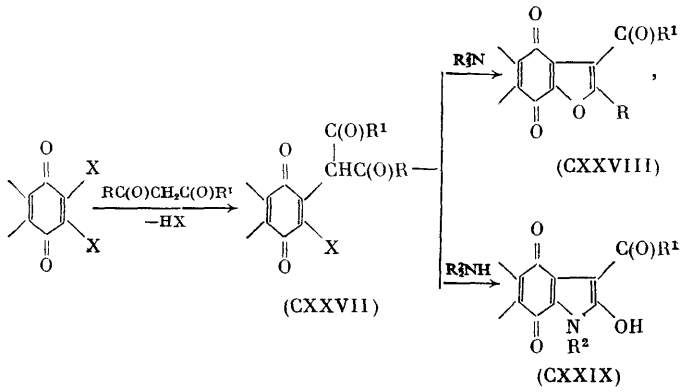
Acetylenes react similarly with halogenoquinones, yielding alkynylquinones in one step.[181]



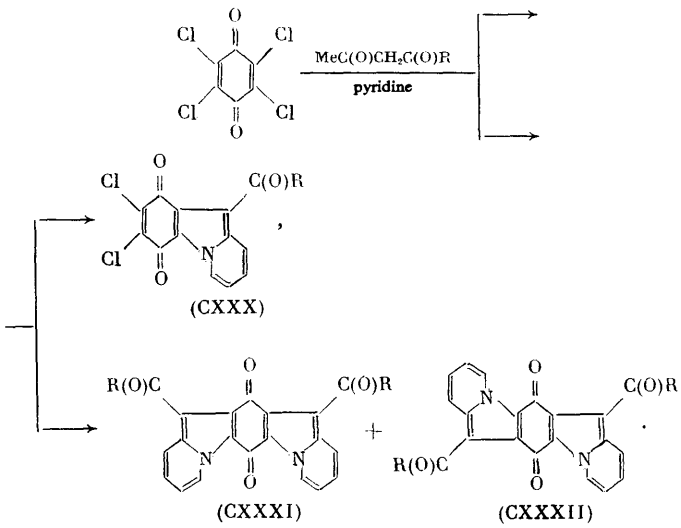
Cyclic hydrocarbons having a labile hydrogen also interact with halogenoquinones by nucleophilic substitution.[182,183]



The reaction of 1,3-dicarbonyl compounds with halogenoquinones is complex. It is initiated by replacement of a halogen to give quinones (CXXVII), which are converted to furan derivatives (CXXVIII) on treatment with tertiary amines; primary amines, however, yield indole derivatives (CXXIX).[180,184–186]



Many of the resulting furans (CXXVIII) and indoles (CXXIX) are biologically active. A rare three-component condensation is achieved by interaction of halogenoquinones with 1,3-dicarbonyl compounds and pyridine. Pyridoindoloquinones (CXXX) or benzodiindolizinequinones (CXXXI and CXXXII) are formed depending on the proportion of the reactants.[180,187]



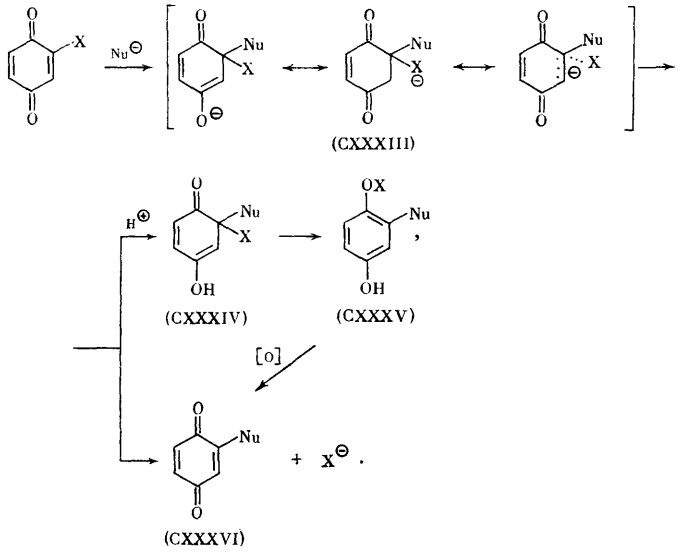
The overall scheme for this three-component conversion is exemplified by the reaction of 2,3-dichloro-1,4-naphthoquinone with indan-1,3-dione and pyridine.[188]

4. Reactions with *P*-nucleophiles

Detailed information on the interaction of quinones with organophosphorus compounds, where the phosphorus atom is the nucleophilic centre, is available in an earlier review.[135] It suffices only to point out that nucleophilic substitution is generally achieved by interaction of a phosphorus(III) compound (phosphines, phosphites, amidophosphites) with polyhalogenoquinones (e. g. chloranil, 2,3-dichloro-1,4-naphthoquinone). The substitution product is either a bipolar ion or a phosphonate with a quinone residue.[135]

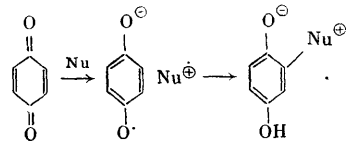
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Sometimes quinones are viewed as α,β-unsaturated carbonyl compounds. However, such is unrealistic, even in a formal sense, as the quinone system cannot be considered strictly as a carbonyl-conjugated structure, nor its chemical properties studied systematically on this basis. As an overview of the multitude of quinone reactions, the following should be borne in mind: 1) the main distinguishing feature of quinones and their derivatives is their readiness to form energetically favourable aromatic or semiquinoidal systems; 2) an important chemical property of quinones is their ability to exchange ring substituents without destroying the quinoidal system; 3) mechanistically, the majority of quinone reactions proceed by a heterolytic pathway with the formation of addition or substitution products. Nucleophilic reactions can be represented by a general scheme, the first step of which is unique for both Ad_N and S_N mechanisms. This comprises addition of the nucleophile, Nu^-, to a carbon atom of the ring with formation of a resonance structure (CXXXIII). Its stabilisation is achieved either by addition or substitution.



If the substituent (X) is a poor leaving group, e. g. hydride anion, then a proton (H^+) adds to the intermediate, followed by isomerisation of the adduct (CXXXIV) with formation of hydroquinone (CXXXV). With highly nucleofugal substituents (X = Hal^-, RO^-, R_2N^-), the intermediate (CXXXIII) is stabilised by cleavage of anion, X^-, and formation of quinone (CXXXVI). The arrow linking compounds (CXXXV) and CXXXVI) signifies that hydroquinones (CXXXV) with donor substituents are readily oxidised to the corresponding quinones (CXXXVI).

In certain cases, single electron transfer from the nucleophile to the quinone can be achieved with formation of a radical pair, the recombination of which leads to the formation of a betaine.[135]



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