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Stable Methylenequinones

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Data obtained in studies on the chemistry of a vigorously developing class of conjugated compounds (methylenequinones) are surveyed. The structure of these compounds and the influence of substituents on their properties and reactivity are discussed. Typical methods of synthesis of methylenequinones are described and the mechanism of their formation as well as the interconversions of methylenequinones and the corresponding phenols in radical and heterolytic reactions are considered. The bibliography includes 144 references.

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I. INTRODUCTION

Methylenequinones (quinone methides) are labile organic compounds belonging to the class of unsaturated cyclic conjugated ketones. The study of the properties of these substances has developed vigorously during the last decade primarily owing to the specificity of their structure, high reactivity, and the role which they play in many chemical and biochemical reactions.[1-3] Methylenequinones form part of the composition of plant pigments,[4] participate in the metabolism of natural products,[5] are used in medicine,[6] and are able to inhibit the thermo-oxidative degradation reactions of polymers.[7] Finally, the chemical properties of methylenequinones and phenols proved to be indissolubly linked, which is manifested most distinctly in the relation between sterically hindered phenols and the corresponding methylenequinones.[8]

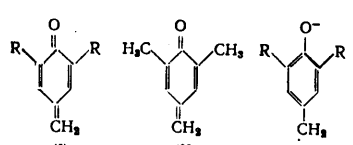
The molecules of methylenequinones are characterised by a high degree of conjugation, lability of the π-electronic bond system, and the capacity for the delocalisation of electrons, which is reflected in the physical properties of methylenequinones and in the marked influence of substituents, particularly those attached to the carbon atom of the methylene unit, on the structure and chemical properties of compounds of this class. This review deals with the methods of synthesis and the properties of stable *para*-methylenequinones.

II. STRUCTURE, STABILITY, AND PHYSICOCHEMICAL PROPERTIES

The simplest methylenequinones are usually unstable. Hitherto they have not been isolated in a pure state. At the instant of formation, these methylenequinones either polymerise or interact with the medium. Their high reactvitiy is due primarily to the characteristic features of their structure. Analysis of calculated data on the structure of the simplest methylenequinones and their closest analogues—quinones and dimethylenequinones (quinodimethanes)—has shown that the ground state of methylenequinones can be both singlet and triplet.[9] The triplet states of *p*-dimethylenequinone and *p*-methylenequinone are biradicals of the dibenzyl or hydroxybenzyl type with a benzenoid (and not quinonoid) aromatic ring and one can therefore speak of the ground singlet (quinonoid) state of these conjugated compounds and of their transition triplet (benzenoid) state. Calculations on the singlet and triplet states of the *p*-dimethylenequinone molecule have shown[9-11] that in the former case it is diamagnetic and has a quinonoid structure, while in the latter state the molecule should be paramagnetic and should have a benzenoid structure with similar C–C bond lengths in the six-membered ring. The difference between the energies of the singlet and triplet states of *p*-dimethylenequinone is approximately 25 kJ mol^{-1}, so that *p*-dimethylenequinones can exist in the singlet state only at low temperatures, which is consistent with experimental data.[11] On the other hand, calculations have shown[9] that *p*-benzoquinone exists virtually in the singlet state and the probability of its transition to the triplet state is lower by a factor of 2.7 x 10^5 than for *p*-dimethylenequinone.

p-Methylenequinone occupies an intermediate position. The probability of its singlet–triplet transition is only 47 times lower than for *p*-dimethylenequinone and the difference between the energies of the singlet (quinonoid) and triplet (benzenoid) states is about 34 kJ mol^{-1}.[9] Thus the possibility of the conversion of *p*-methylenequinone into a biradical of the hydroxybenzyl type in the absence of factors stabilising the quinonoid bond system is fairly high. This in fact explains why the simplest (unsubstituted) methylenequinone does not exist under the usual conditions and polymerises during its preparation.[12-14]

The stability of methylenequinones increases significantly when one of the reaction centres, for example the oxygen atom, is sterically shielded. Naturally, this effect is manifested to the maximum extent for 2,6-di-t-butylmethylenequinone (I), which dimerises (at a concentration of 0.01 M) 10^3 times more slowly than 2,6-dimethylmethylenequinone (II).[15] The methylenequinone(I) can be isolated in a pure state, although at room temperature it undergoes an irreversible singlet–triplet transition in the course of several minutes with the subsequent formation of characteristic triplet methylenequinone conversion products.[16] The EPR spectrum of the compound in thetriplet state, measured at a concentration of 0.25 M, consists of three triplets and corresponds to the structure of the biradical (III):[17]



(I) (II) (III)

R = t-butyl group

The high degree of stabilisation of the quinonoid bond system of the methylenequinone is obtained as a result of the increase in the conjugation chain of the molecule. This effect is significant for

α-substituted (at the methylene unit) methylenequinones. Thus αα-dicyano-[18] and αα-diphenylmethylenequinones[19] can also be isolated in a pure state; they are less reactive than the methylenequinone (I).

Theoretically, on the basis of the calculation of the electron density and the bond order in the molecule of the simplest methylenequinone by the LCMO method, one may expect three $\pi-\pi^*$ transitions.[20] The most intense ($\lg\varepsilon = 4.05$) long-wavelength transition, corresponding to the wavelength $\lambda_{max} = 287$ nm ($\lambda_{max} = 282$ nm has been found experimentally), is associated with polarisation in the direction parallel to the symmetry axis of the methylenequinone molecule. Two other transitions, with $\lambda_{max} = 274$ nm and $\lambda_{max} = 229$ nm, associated with the polarisation of the molecule in the direction at right angles to the longitudinal symmetry axis, should have a low intensity. They have not been confirmed experimentally.[21] The difference between the λ_{max} of the substituted methylenequinones and the unsubstituted methylenequinone depends on the number and nature of the substituents and is an additive quantity. For any substituted methylenequinones, one can therefore calculate the maximum for the allowed $\pi-\pi^*$ transition from the positions and number of the substituents in the methylenequinone molecule. The wavelength of the main absorption maximum of the substituted methylenequinone is equal to the sum of the wavelengths of the main absorption maximum of the unsubstituted methylenequinone ($\lambda_{max} = 282$ nm) and the increments $\Delta\lambda$ characteristic of the substituents.[22] As can be seen from the data in Table 1, the α-substituents in the methylene unit of the methylenequinone molecule induce a much greater bathochromic shift than the ortho-substituents in the six-membered ring. Such additivity is in fact characteristic of methylenequinones, while in substituted benzoquinones the dependence of the bathochromic shift on the number and nature of the substituents is non-linear.[23].

Table 1. The increments due to the substituents for the calculation of the principal absorption maxima in the spectra of substituted methylenequinones.[8,22]

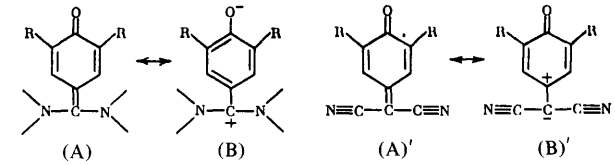


Substituent	Position	Δλ, nm	Substituent	Position	Δλ, nm
CH_3	2(6)	4	$HOCH_2CH=$	4	16
$(CH_3)_3C$	2(6)	4	$HOCOCH=$	4	20*
Br	2(6)	12	$C_6H_5CH=$	4	62*
CH_3O	2(6)	15	$(NC)_2CH=$	4	53
$CH_3CH=$	4	18*	$C_2H_5(CN)CH=$	4	41
$CH_3CH_2CH=$	4	18			
$(CH_3)_2C=$	4	36		4	137*
$CH_3OCH=$	4	40*			
$(CH_3)_2NCH=$	4	95*		4	67*
$NCCH=$	4	28			
				4	90*

*From Ershov et al.[8]

Semiquantitative data on the π-electron delocalisation in the ground state have been obtained in a study of the ^{13}C NMR spectra of methylenequinones.[24,25] Analysis of the ^{13}C chemical shifts in the six-membered ring and in the methylene group of αα-disubstituted 2,6-di-t-butylmethylenequinones and 2,6-dialkyl-αα-diphenylmethylenequinones showed that the effect of the *ortho*-substituents arises predominantly (to the extent of approximately 80%) via the inductive mechanism, while the influence of α-substituents is associated mainly with conjugation (63–79%).

Depending on the electronegativity of the α-substituents, the carbonyl group of the methylenequinone can function both as an electron acceptor and an electron donor, which is reflected in the two diametrically opposed limiting structures (B) and (B)′, for example, of the molecules of αα-diamino- and αα-dicyano-2,6-di-t-butylmethylenequinones, in which the extent of intramolecular interaction is a maximum:[24]



(A) (B) (A)′ (B)′

On the other hand, in most of the other known methylenequinones the electron distribution obeys the rules for weak charge-transfer complexes, the energy transfer as a result of the intramolecular interaction is proportional to an ionisation potential function of the donor component molecule: $h\nu_i = \gamma I_d - \delta$, where ν_i is the absorption frequency for the ith bond, I_d the ionisation potential of the donor component of the methylenequinone molecule, and γ and δ are constants characterising the acceptor component of the methylenequinone molecule. The γ and δ constants are invariant for a series of αα-disubstituted 2,6-di-t-butylmethylenequinones (the correlation coefficient is $r = 0.967$).[24]

Measurement of the dipole moments of substituted methylenequinone in both ground (μ) and excited singlet (μ*) states confirmed the lability of the conjugated bond system in methylenequinone, which can be expressed by the corresponding contribution of the dipolar structure of type (B). In the ground state, this contribution is 9–18% and depends on the steric effects of the *ortho*-substituents, while in the first excited singlet state it increases to 25–40% and depends less on the character of the *ortho*-substituents in the methylenequinone molecule.[26]

The quantity $\Delta\mu = \mu^* - \mu$, characterising the degree of delocalisation of π electrons, has been found from the calculation and experimental data referring to the variation of the absorption maximum for a series of 2,6-dialkyl-αα-diphenylmethylenequinone in various solvents. The introduction of substituents into the methylene ring increases the dipole moment μ, whose value is correlated with the electrophilic substituent constants σ_p^+, including the inductive and conjugation effects:[27]

$$\mu = [(-7.55 \pm 1.2)\,\sigma_p^+ + 10.94] \cdot 10^{-30}\ (r = 0.993,\ n = 6)$$

The vibrational spectra of methylenequinones are close to those of quinones and quinolide compounds.[28,29] The IR spectra of methylenequinones contain the vibration frequencies of the conjugated carbonyl group, the latter being manifested as a rule by a doublet, and the intensity and positions of the frequencies in the spectrum depend on the nature of the α-substituents.[30,31]

The application of model computational and experimental research methods makes it possible to interpret from a quantitative standpoint the IR spectra of various 2,6-dialkyl-αα-diphenylmethylenequinones and α-substituted 2,6-di-t-butylmethylenequinones.[32,33] It was found that the frequency ν_{CO} can be used to analyse the electronic interactions and the reactivities of the methylenequinones containing various substituents. The frequency ν_{CO} in the IR spectra of methylenequinones is correlated with the electrophilic constants of the substituents:

$$\Delta\bar{\nu}_{CO} = 9.41\ (\pm 0.58)\,\sigma_p^+ + 3.20\ (r = 0.973)$$

and the electronic effects therefore exert a decisive influence on ν_{CO} in methylenequinones. Furthermore, a two-parameter correlation, based on the inductive (σ_I) and the resonance components of the σ constant, has been established, which indicates approximately equal

contributions of the inductive and conjugation effects to the mechanism of the intramolecular interaction via the system of conjugated double bonds in the ground state of methylenequinones:

$$\Delta\bar{\nu}_{CO} = 9.47\,(\pm 2.03)\,\sigma_I + 9.50\,(\pm 0.79)\,\sigma_R^+ + 3.02\ .$$

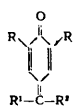
The experimental results were confirmed by a calculation taking into account the dependence of $\bar{\nu}_{CO}$ on the solvent polarity (Table 2). By analysing the vibration frequencies of the carbonyl group and the integral intensities for a series of αα-diphenylmethylenequinones, the contribution of the steric effects to the mobilities of the electrons has been calculated for 2-monoalkyl- and 2,6-dialkylmethylenequinones:[33]

$$\bar{\nu}_{CO} = 35.6\Sigma\sigma_I - 9.1\Sigma\omega + 1625.5\,(r = 0.982)\,,$$

$$A_{CO}^{1/2} = -33.2\Sigma\sigma_I - 1281\Sigma\omega + 141.1\,(r = 0.942)\,,$$

where ω is a quantity proportional to the van der Waals radii of the substituent and $A_{(CO)}$ is a quantity proportional to the integral intensity of the vibration frequency of the carbonyl group.

Table 2. The experimental and calculated vibration frequencies of the carbonyl group in α-substituted 2,6-di-t-butylmethylenequinones.[30,32]

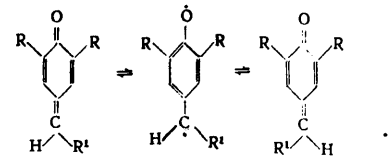


R^1	R^2	ν_{CO}, cm^{-1}	
		calculation	experiment
H	H	1621.7	1615*
H	OCH_3	1614.4	1616
H	CH_3	—	1618
H	C_6H_5	1619.5	1618, 1621*
H	CN	—	1635, 1632*
H		—	1610
CH_3	CH_3	—	1616.5
CH_3	CN	1625.0	—
	CN	—	1635
		—	1592

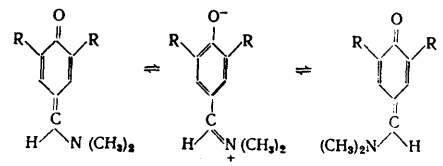
*From Volod'kin and Ershov.[30]

The vibration frequencies of the carbonyl group and the integral intensities diminish with increase in the van der Waals radii of the *ortho*-substituents, the delocalisation of the electrons due to the "*ortho*-effect" in 2,6-dialkylmethylenequinones being approximately 30% higher than in the 2-mono-substituted methylenequinones.

The specificity of the structure and properties of methylenequinones are also manifested in the ^{1}H NMR spectra of these compounds, in the first place as a consequence of the effect due to the hindered rotation about the exocyclic C=C bond.[34,35] This effect was observed for the first time in the analysis of the ^{1}H NMR spectra of substituted stilbenequinones[36] in which the non-equivalence of the *meta*-protons and the protons of the *ortho*-substituents is manifested. The non-equivalence of the ring protons of methylenequinones is associated with the different substituents in the α-position. At room temperature rotation around the exocyclic C=C bond is not observed. The study of the temperature dependence of the ^{1}H NMR spectra of α-substituted methylenequinones showed that the barrier to the intramolecular rotation about the C=C bond in such compounds is fairly high and the activation energy for this transition is greater than 105 kJ mole^{-1}. It has been suggested[35] that the rotation about the exocyclic C=C bond can take place via a biradical transition state:



According to the data of Mannchreck and Kolb,[37] the free electron pair of the nitrogen atom in the molecule of 2,6-di-t-butyl-α-dimethylaminomethylenequinone is coplanar with the cyclohexadiene ring. The ^{1}H NMR spectrum of this methylenequinone is temperature dependent as a consequence of the effects considered above, while the calculated low barrier to the intramolecular rotation about the C=C bond (60.7 kJ mol^{-1}) and the high barrier to the rotation about the C−C single bond (52 kJ mol^{-1}) show that the rotation about the C=C bond takes place via a dipolar transition state, which agrees well with the data considered previously:[24]

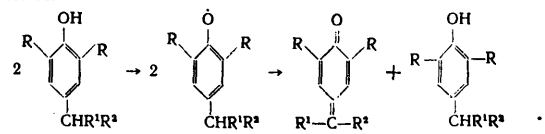


Thus analysis of the physicochemical data on the structure and the influence of substituents on the conjugated system of double bonds in methylene quinones permits a fairly clear-cut formulation of the condition for the stability of methylenequinones (the presence of substituents in the six-membered ring and at the carbon atom of the methylene unit) and makes it possible to deduce the reactivity of these compounds, a characteristic feature of which should be both radical reactions and electrophilic and nucleophilic 1,6-addition reaction by virtue of the presence in the molecule of two reaction centres: the nucleophilic centre at the oxygen atom and the electrophilic centre at the carbon atom of the methylene unit.[38]

III. THE FORMATION OF METHYLENEQUINONES

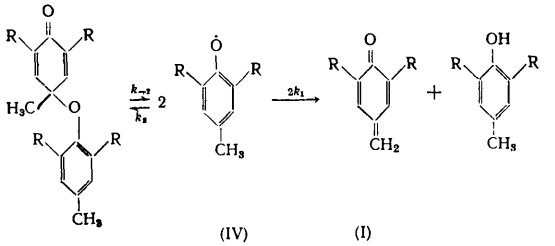
The relation between methylenequinones and phenols is manifested primarily in their interconversions caused by various chemical reagents and the methods of synthesis of stable methylenequinones are therefore mainly based on the reactions of substituted phenols.

The commonest method of synthesis of methylenequinones consists in the oxidation of phenols by variable-valence metal compounds (one-electron oxidation).[39-44] In the presence of α-hydrogen atoms in the molecule of the initial phenol, the phenoxy-radical formed initially disproportionates into methylenequinone and the initial phenol:



The kinetics of the decomposition of the majority of α-hydrogen-containing phenoxy-radicals are bimolecular. However, in the case of the 2,6-di-t-butyl-4-methylphenoxy radical (IV), the kinetics proved to be more complex, which has been the subject of many years' discussion concerning the mechanism of its decomposition. According to the initial view, the phenoxy-radical (IV) isomerises via a first-order reaction to a radical of the hydroxybenzyl type, whose recombination leads to the formation of dimeric compounds.[45-58] However, more recent data[49] confirm that the decomposition mechanism of the radical (IV) via the disproportionation reaction is general and it was found that the order of this reaction depends on the

concentration of the radical (IV). Such dependence is associated with the dimerisation reaction of the radical (IV) which takes place as a parallel process, which is reflected in the relation between the order of the reaction and the concentration of this radical:[50]

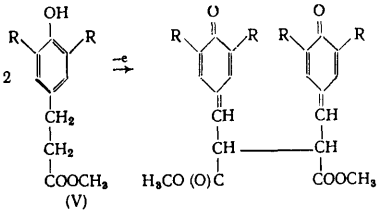


(IV) (I)

It was shown that, when $4K_2[PhO^{\cdot}] \gg 1$, where $K_2 = k_2/k_{-2}$, the decomposition of PhO$^{\cdot}$ is described by a first order law with $k_{eff} = k_1/2k_{-2}$, and, when $4K_2[PhO^{\cdot}] \ll 1$, the decomposition of PhO$^{\cdot}$ is a second order process with $k_{eff} = 2k_1$.

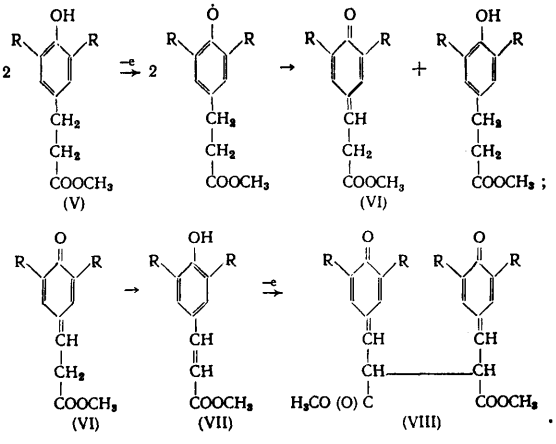
The duration and temperature of the oxidation of the initial substituted phenols are important factors influencing the attainment of the maximum yield of methylenequinones, which is usually associated with the high reactivity of the methylenequinones themselves and their involvement in parallel reactions. Thus the methylenequinone (I) is formed on oxidation of 2,6-di-t-butyl-4-methylphenol (concentration 0.15 M) after 10–15 min in 97–98% yield.[51] The increase in the duration of oxidation to 3–4 h lowers the yield of the methylenequinone (I) to 50% at the expense of its consumption via the spontaneous disproportionation reaction.

The processes in the oxidation of phenols containing hydrogen atoms in the β-position of the carbon chain can vary. For example, whereas the oxidation of 2,6-di-t-butyl-4-(β-phenylethyl)phenol results in the formation of only the corresponding methylenequinone,[52] oxidative dimerisation is observed in the oxidaion of β-(3,5-di-t-butyl-4-hydroxyphenyl)propionic acid:[53,54]



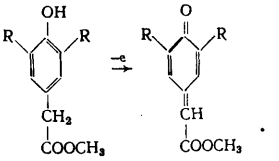
(V)

The study of the mechanism of the oxidation of methyl β-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (V) showed that the methylenequinone (VI) formed in this case is unstable and isomerises spontaneously to the corresponding vinylphenol (VII), whose subsequent oxidation yields the oxidative dimerisation product (VIII). The overall mechanism of the oxidation of the ester (V) by one-electron oxidants can therefore be represented as follows:[55]

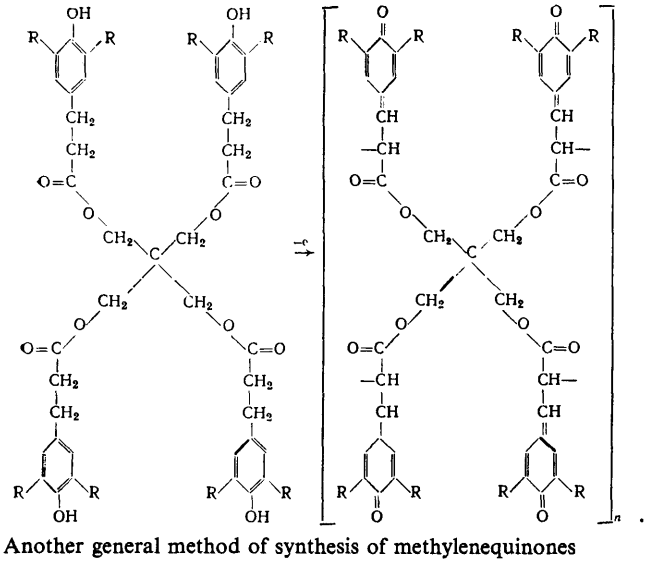


(V) (VI) (VI) (VII) (VIII)

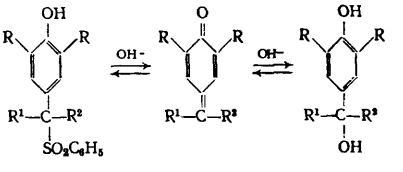
It is noteworthy that, in the oxidation of methyl (3,5-di-t-butyl-4-hydroxyphenyl)acetate, which contains no mobile β-hydrogen atoms, the stable 2,6-di-t-butyl-α-methoxycarbonyl methylenequinone is formed:[51]



Analogous reactions take place also with certain industrial phenolic antioxidants containing several fragments of a sterically hindered phenol in the molecule, for example in the oxidation of the pentaerythrityl ester of β-(3,5-di-t-butyl-4-hydroxyphenyl)propionic acid.[7] It was shown kinetically that in this case the destruction of the phenoxy-radicals takes place as a result of the intramolecular reactions of a biradical.[50,56]



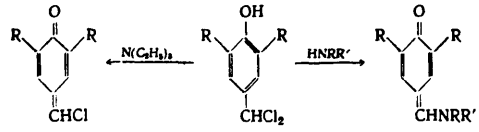
Another general method of synthesis of methylenequinones involves treatment with bases of phenols containing in the benzyl position halogen atoms,[57] the sulpho-group,[58-61] or the hydroxy-group.[62-64] This reaction can be regarded as a special case of the solvolysis of the phenol derivatives indicated, which terminates with the formation of a methylenequinone.[58,59] For example, the methylenequinone (I) is obtained in the reaction of 3,5-di-t-butyl-4-hydroxybenzyl halide with a trialkylamine.[52,56,65] In the general case, the solvolytic reaction in the presence of alkali is reversible and the reactivity of the initial phenols depends on their ability to form a methylenequinone, while the equilibrium constants are determined by the nature of the substituents in the benzyl position:[58,59]



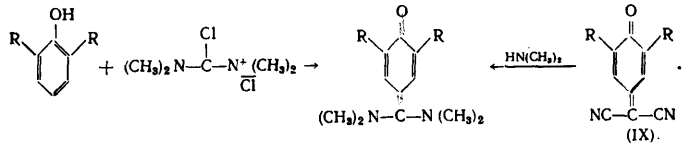
Consequently the yield of the methylenequinone is related to the equilibrium conditions in two reactions.[59]

The interaction of equimolar amounts of di-t-butyl-4-hydroxybenzyl halides with secondary amines also involves the intermediate formation of the corresponding methylenequinones, which are capable of reacting with an excess of the amine to form 3,5-di-t-butyl-4-hydroxybenzylamines.[66,67] However, the reactions of 3,5-di-t-butyl-4-hydroxybenzylidene dichloride with secondary amines terminate

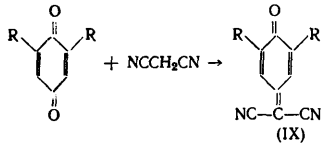
with the formation of 2,6-di-t-butyl-α-(*NN*-dialkylamino)methylenequinones; the above reaction with a tertiary amine yielded 2,6-di-t-butyl-α-chloromethylenequinone:[57]



A number of specific reactions leading to the formation of 2,6-di-t-butyl-α-(*NN*-dialkylamino)methylenequinones are known; for example, the condensation of 2,6-di-t-butylphenol with bis(dimethylamino)methyl chloride[68] and the aminolysis of 2,6-di-t-butyl-αα-dicyanomethylenequinone:[68,69]

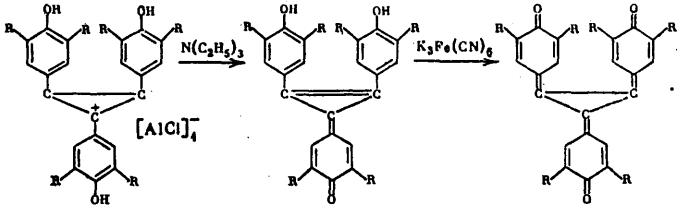


The methylenequinone (IX) has been obtained by condensing 2,6-di-t-butylquinone with malonodinitrile:[69,70]



The interaction of dichlorodiphenylmethane with 2,6-di-t-butylphenol leads to the formation of 2,6-di-t-butyl-αα-diphenylmethylenequinone.[71] Examples of the formation of αα-diphenylmethylenequinones in photochemical reactions have also been described.[72-75]

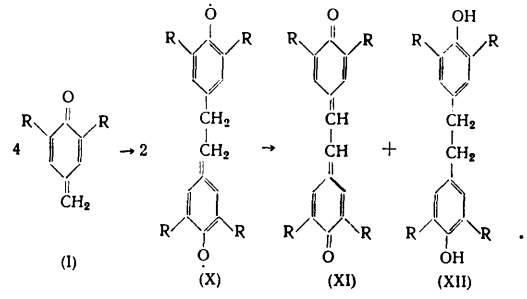
Compounds with a cross-conjugated bond system, which include several structural methylenequinone fragments, constitute a specific group. A general method of synthesis of polymethylenequinones is based on the condensation of 2,6-disubstituted phenols with derivatives of unsaturated cyclic hydrocarbons.[76-87] The complex of tetrachlorocyclopropene with aluminium chloride,[81,83,84,86] the complex of cycloheptatriene with fluoroboric acid,[78,80] and other cyclic unsaturated compounds[82,85] have found wide-scale applications for such purposes. For example, the condensation of 2,6-di-t-butylphenol with tetrachloropropene in the presence of aluminium chloride results in the formation of an adduct with three phenyl molecules, from which a derivative of methylenequinone containing also the aromatic rings of phenol is formed on treatment with a tertiary amine. On treatment with one-electron oxidants, the aromatic rings in such compounds are converted into the cyclohexadiene system with formation of a cross-conjugated bond system:[81]



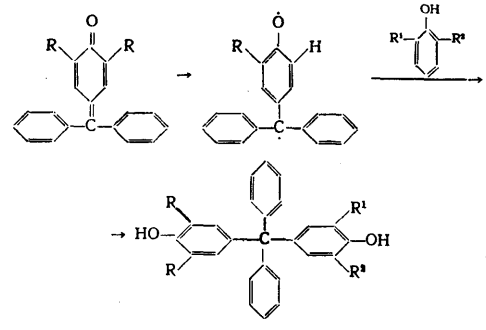
Compounds with such a bond system are relatively stable and can be isolated in a pure state. However, cross-conjugated methylenequinones exhibit very marked oxidising properties and some of them are capable of forming stable radical-anions.[83,84,86,87]

IV. RADICAL REACTIONS OF METHYLENEQUINONES

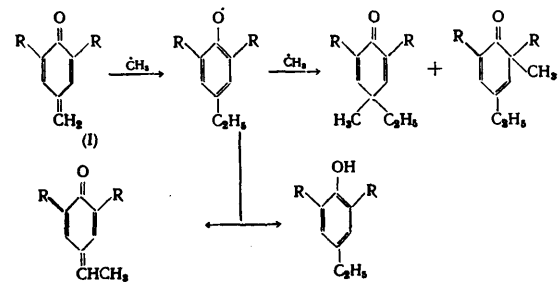
The radical reactions proper of methylenequinones in the form of biradicals (in the triplet state) are characteristic only of the simplest unsubstituted methylenequinones (polymerisation) and the methylenequinone (I), which dimerises spontaneously even in dilute solution with formation of the bisphenoxy-radical (X): Further reactions of this radical lead to a mixture of the stilbenequinone (XI) and dihydroxydiphenylethane (XII):[49,51,56,89]



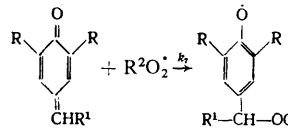
The formation of radical species in the disporportionation of the methylenequinone (I) has been confirmed by EPR.[17] For the stable αα-disubstituted methylenequinones, the singlet–triplet transition can be achieved only in photosensitised reactions. Thus, in the presence of excited benzophenone, 2,6-dialkyl-αα-diarylmethylenequinones react with 2,6-dialkylphenols via a radical mechanism with formation of di(hydroxyaryl)diphenylmethanes:[19]



Apart from the reactions indicated, many methylenequinones are capable of interacting directly with various radicals or of dehydrogenating organic compounds via a radical mechanism. Methylenequinones interact vigorously with alkyl radicals. In the model reaction of the methylenequinone (I) with methylradicals under the conditions of their constant generation as a result of the decomposition of t-butyl hydroperoxide by bivalent iron salts, the radical adds to the carbon atom of the methylene unit of the methylenequinone with formation of an intermediate phenoxy-radical, which is subsequently consumed, fully in conformity with the rules governing the behaviour of phenoxy-radicals, via a disproportionation reaction and via recombination with the methyl radicals present in excess:[56]



The possibility of using methylenequinones in the inhibited oxidation of organic substrates is based on their ability to participate in radical reactions. It follows from kinetic data for the inhibited oxidation of cumene or styrene that methylenequinones react fairly rapidly with peroxy-radicals $RO_2^{\cdot}$:[90]

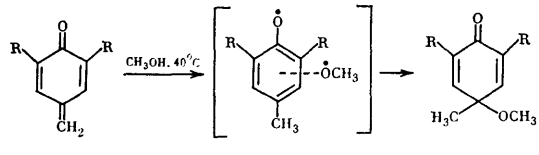


Quantitative estimation of the inhibiting effect of methylenequinones established that the quantity k_7 is independent of the concentration of the methylenequinone and that the phenoxy-radicals formed in this case do not therefore participate in propagating the oxidation chin. Comparison of the values of k_7 for methylenequinones and structurally similar phenols shows that the methylenequinones are somewhat less effective than the phenols in the reaction with phenoxy-radicals (Table 3). However, in this connection attention should be drawn to an interesting fact: the effectiveness of the bismethylenequinone (VIII)—the product of the oxidative dimerisation with the phenolic stabiliser (V)—is approximately equivalent to the effectiveness of the phenol (V) itself. Methylenequinones are effective inhibitors of the radical polymerisation of styrene (concentration 10^{-2} M, initial rate of initiation $w_i = 2.98 \times 10^{-7}$ mol litre^{-1} min^{-1}). The rate constants for the reactions of α-substituted 2,6-di-t-butylmethylenequinones with alkyl radicals are $0.8 \times 10^4 - 1.3 \times 10^5$ litre mol^{-1} s^{-1}, which is higher by 1–2 orders of magnitude than the rate constants for the reactions of the same methylene quinones with alkyl-peroxy-radicals.[91] It follows from the result of the same study that the bismethylenequinone (VIII) is equally reactive in the reactions with both alkyl and alkylperoxy-radicals.

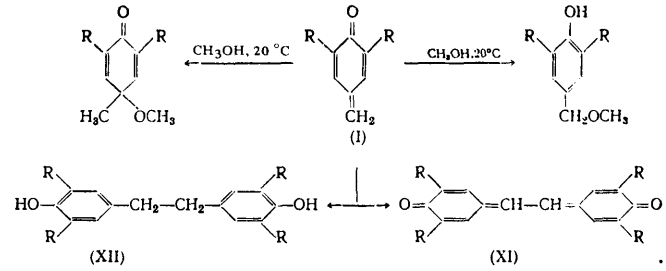
αα-Disubstituted methylenequinones with electronegative substituents do not inhibit the polymerisation of styrene and radical reactions are therefore not characteristic of methylenequinones of this type.

Methylenequinones are also stabilisers of the degradation of high-molecular-weight materials (polymers) and effectively inhibit the oxidation of polyolefins at high temperatures.[7,56] The inhibition of the thermo-oxidative degradation of polymers by methylenequinones is due to their ability to interact with both peroxy- and alkylradicals. This property in methylenequinones is of fundamental importance for the specific synthesis of effective stabilisers in the class of sterically hindered phenols, since the formation of methylenequinones in the primary step of the interaction of the polymeric radical $RO_2^{\cdot}$ with phenolic antioxidants depends on the structure of the sterically hindered phenol and the character of the substituents.

The simplest methylenequinones and the methylenequinone (I) are also capable of dehydrogenating certain organic compounds. For example, the methylenequinone (I) reacts with methanol in dilute solutions at 40 °C to form the methyl ether of the corresponding quinol, the phenoxy-radical produced being directly responsible for the formation of the ether:[51,92]

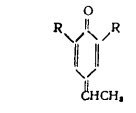
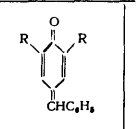
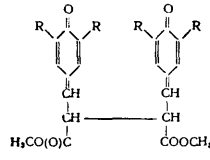
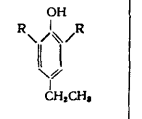
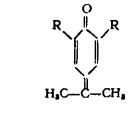
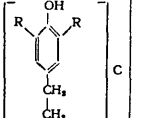


In addition, the formation of 3,5-di-t-butyl-4-hydroxybenzyl methyl ether, possibly via the competing reaction involving the heterolytic 1,6-addition of methanol, is observed. Together with the products of the interaction of the methylenequinone (I) with methanol indicated above, the characteristic products of the reactions of triplet methylenequinone are also formed—the stilbenequinone (XI) and dihydroxydiphenylethane (XII):



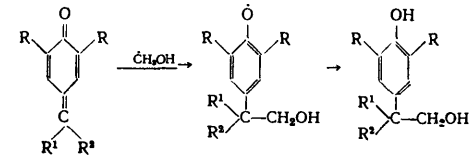
In the presence of catalytic amounts of an acid or alkali, only 3,5-di-t-butyl-4-hydroxybenzyl methyl ether is formed in this reaction.[93]

Table 3. The rate constants for the reactions of methylenequinones and phenols with peroxy-radicals $RO_2^{\cdot}$ in the inhibited oxidation of cumene and styrene.*

Inhibitor	k_7, litre mol^{-1} s^{-1}		Inhibitor	k_7, litre mol^{-1} s^{-1}	
	cumene	styrene		cumene	styrene
	$5.8 \cdot 10^2$	$1.4 \cdot 10^3$		—	$1.8 \cdot 10^2$
	$4.0 \cdot 10^4$	—		$4.0 \cdot 10^4$	$1.0 \cdot 10^3$
	$1.6 \cdot 10^4$	—		$2.9 \cdot 10^4$	—

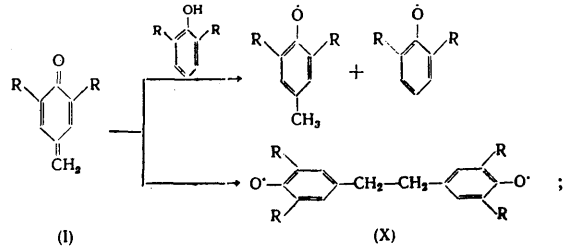
*Determined from the kinetics of the absorption of oxygen in the inhibited oxidation of the hydrocarbons in the presence of an oxidation initiator—azobisisobutyronitrile—at 60 °C.[90]

On irradiation with UV light (mercury lamp), methylenequinones react with methanol somewhat differently. According to the data of Yang et al.[94] and Matsuura and Ogura,[95] when a solution of the methylenequinone (I) or 2,6-di-t-butyl-αα-diphenylmethylenequinone (XIII) in methanol is irradiated, radicals are formed initially from methanol and then react with the methylenquinones. The reaction also proceeds via the phenoxy-radical formation stage:

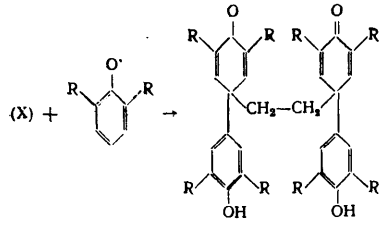


The formation of characteristic radical products has also been noted in the interaction of the methylenequinone (I) in the triplet state with 2,6-di-t-butylphenol[96] and vinylphenols.[97] These are multistage reactions. The phenol is initially dehydrogenated by the

methylenequinone with formation of two phenoxy-radicals, for example, the phenoxy-radical (V) and the 2,6-di-t-butylphenoxy-radical. As noted above, the methylenequinone (I) dimerises spontaneously with formation of the biradical (X), whose recombination with the 2,6-di-t-butylphenoxy-radical leads to the formation of compound (XIV) in 17% yield:[96]

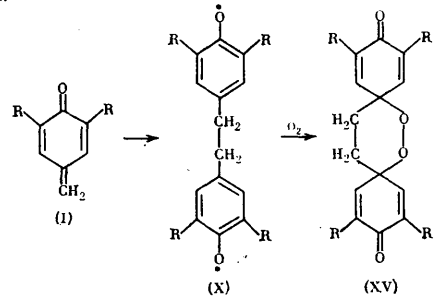


(I) (X)



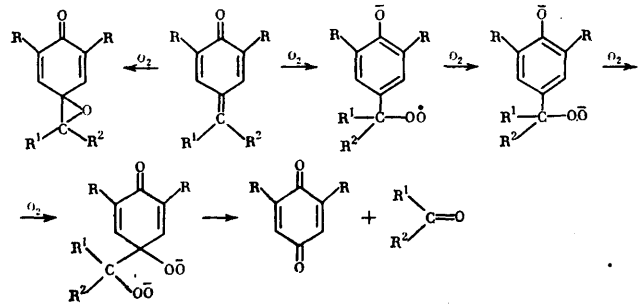
(XIV)

The majority of the known stable methylenequinones are inert in relation to oxygen. However, examples of the catalytic interaction of oxygen with substituted methylenequinones and its non-catalytic reaction with the methylenequinone (I), as a result of which the cyclic peroxide (XV) of the quinolide type is produced, are known. In the given instance, the biradical (X) participates in the reaction with oxygen:[98]



(I) (X) (XV)

In the catalytic oxidation of alkylmethylenequinones, the oxygen adds initially to the methylene carbon, as a result of which a mixture of oxygen-containing compounds is formed: quinols, the corresponding hydroperoxides, and other products.[88,99,100] For example, in the presence of cobalt compound, the reactions considered have a multistage mechanism and the final products are formed as a result of the occurrence of several stages involving the consecutive oxidation and fragmentation of the intermediate relatively unstable radical-ions, dianions of the quinolide type or having an aromatic structure:[101]



The selectivity of this oxidation depends on the nature of the catalyst and the solvent and temperature.

The typical radical reactions examined above are in fact characteristic of the biradical structure of methylenequinones. On the other hand, methylenequinones exhibit the properties of unsaturated carbonyl compounds with their characteristic heterolytic reactions. An example of a reaction characterising the methylenequinone system as a whole is the stepwise electrochemical reduction. The electron, interacting with the substrate, has the properties of both a radical and a nucleophile. As a nucleophile, the electron interacts in the course of the one-electron electrochemical reduction with the overall π-system of the methylenequinone molecule and passes to the lowest unoccupied molecular orbital. The spin density in the radical-anion formed is localised at the methylene carbon atom[102] and the latter therefore possesses the typical properties of radicals of the hydroxybenzyl type with their characteristic dimerisation processes.[51,56] On the other hand, in the initial step of the interaction between the methylenequinone and the electron, the general properties of methylenequinones as unsaturated carbonyl compounds are exhibited and these properties depend to a large extent on the presence and nature of the substituents in the methylenequinone molecule. For this reason, the electrochemical data for methylenequinones will be examined below in the Section devoted to the heterolytic reactions of these compounds.

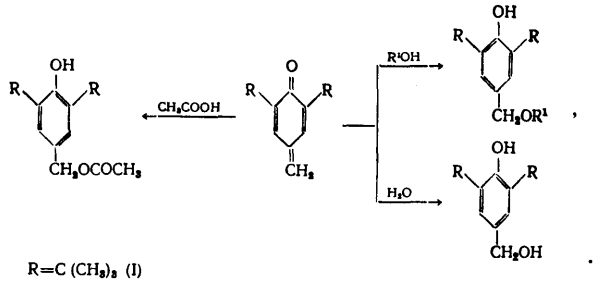
V. HETEROLYTIC 1,6-ADDITION REACTIONS

By virtue of the presence in the conjugated system of atoms with different electronegativities, the methylenequinone molecule contains two reaction centres: a nucleophilic centre which consists of the oxygen of the carbonyl group and an electrophilic centre which consists of the carbon of the methylene unit. Depending on the nature of the attacking agent, the reaction can be directed initially to either of the centres indicated. In both cases the result of the reaction is the same—1,6-addition with formation of phenol derivatives having functional group substituents. Nautrally, the reactions with electrophiles begin with the attack on the most electronegative oxygen atom of the carbonyl group incorporated in the conjugation system of the methylenequinone molecule. 2,6-Disubstituted methylenequinones readily react via the mechanism indicated with many electrophiles, which leads to different phenol derivatives with functional group substituents. Protic acids, water, and alcohols react with alkylmethylenequinones via the same pathway.

In dilute solutions, the methylenequinones (I) and (II) react with alcohols via a pseudofirst-order process and the rate of the latter depends quantitatively on the pK_a of the alcohols.[15,103-105] The hypothesis that associated alcohol species participate in the reaction has been justified kinetically.[105] The methylenequinone (II) is more reactive, its reaction, at a concentration of 10^{-2} M, with methanol being 550 times faster than that of the methylenequinone (I).[15] The rate constant for the reaction of the methylenequinone(II) with t-butyl alcohol (k = 1.2 x 10^{-8} s^{-1}) is smaller almost by three orders of magnitude than in the case of methanol (k = 3 x 10^{-5} s^{-1}) or ethanol (k = 4.5 x 10^{-5} s^{-1}); this methylenequinone reacts with acetic acid at a higher rate (k = 1.35 x 10^{-4} s^{-1}). The dependence of the rate of reaction of the methylenequinone (II) with water on its concentration corresponds to a fractional reaction order, because of the exclusive involvement of associated water species in the reaction.[105]

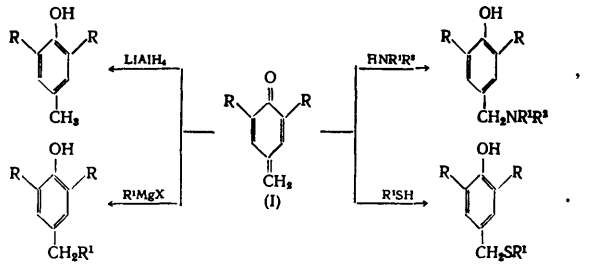
The kinetic features, examined above, of the reactions of 2,6-disubstituted methylenequinones with alcohols, protic acids, and water are valid for dilute solutions at a temperature not higher than 20 °C. Under these conditions, methylenequinones exhibit the properties of unsaturated ketones with their characteristic 1,6-heteroaddition

reactions:

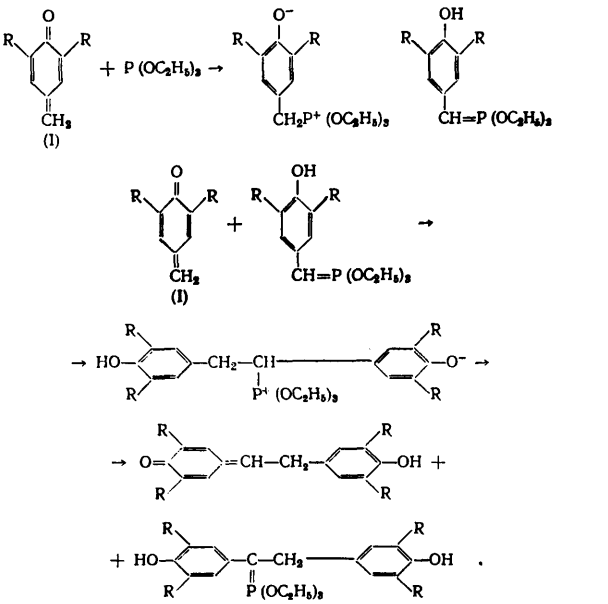


R=C (CH$_3$)$_3$ (I)
R=CH$_3$ (II)

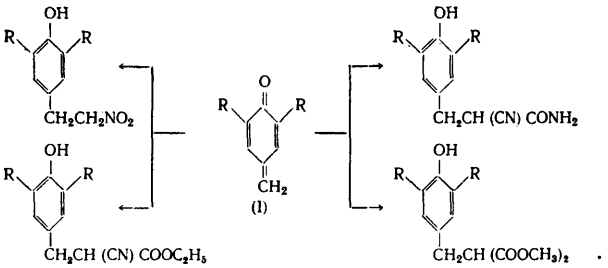
Different workers have investigated most widely the reactions of the methylenequinone (I). which is formed as an intermediate in nucleophilic reactions and on oxidation of a number of derivatives of sterically hindered phenols.[15,30,88,93,106,107] Initially the addition of the nucleophilic species to the methylene carbon atom of the methyl-enequinone molecule also induces the conversion of the quinonoid bond system into an aromatic hydroxy-system and leads to the same reaction product as the initial addition of the proton of the acid reagent. Typical examples of such reactions are those of the methylenequinone (I) with mercaptans, amines, and Grignard reagents, the reduction by alkali metal hydrides, and other reactions:[30,108-112]



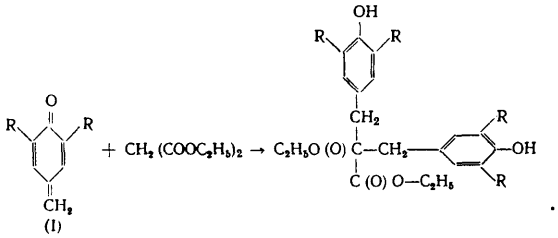
The methylenequinone (I) reacts specifically with triethyl phosphite. This is a multistage reaction:[113]



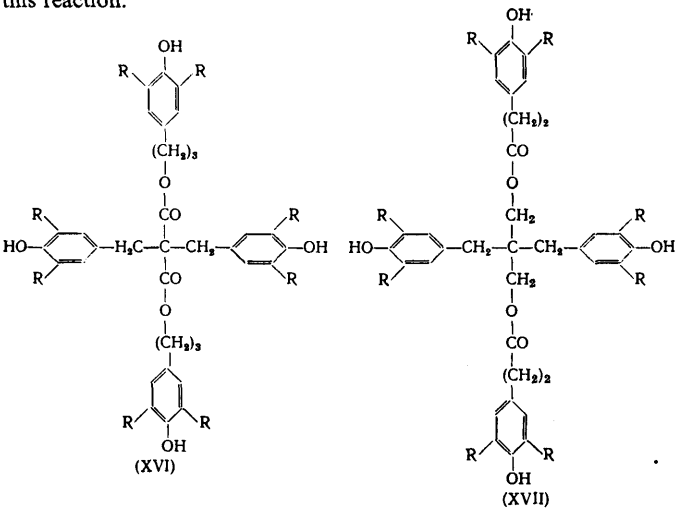
However, as a rule, in most reactions of methylenequinones with nucleophiles a high selectivity is retained, which makes it possible to use them for the synthesis of a wide variety of phenols with functional group substituents, in the first place in the synthesis of antioxidants for the stabilisation of polymers[8,108] and in biological research.[8,114] Thus nitromethane, malonic ester, cyanoacetamide, and cyanoacetic ester add to the methylenequinone(I) with a high degree of selectivity:[115,116]



The nature of the catalyst plays a significant role in the process selectivity. For example, in the presence of potassium t-butoxide, the methylenequinone (I) reacts with malonic ester to form a 1 : 1 adduct, while in the presence of sodium methoxide a 2 : 1 adduct is formed, namely bis(3,5-di-t-butyl-4-hydroxybenzyl)malonic ester:[116,117]



Effective polymer stabilisers (phenozans) have been obtained by this reaction:[117,118]

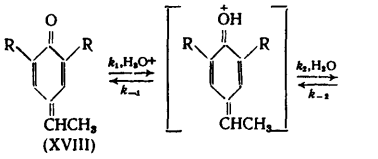


These structurally similar stabilisers are interesting because they behave differently in oxidation by one-electron oxidants. Whereas the oxidation of compound (XVI) leads to the formation of a stable methylenequinone, the oxidation of compound (XVII) involves oxidative dimerisation leading to an increase in the molecular weight of the antioxidant, which significantly improves its thermoprotective properties.[51]

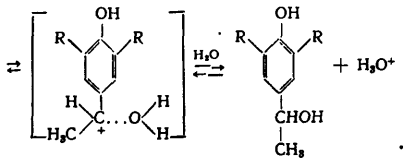
1. α-Alkylmethylenequinones

The homologues of methylenequinones containing alkyl substituents, the carbon atom of the methylene unit and t-butyl groups in the six-membered ring are relatively stable in a pure states. Reactions in the triplet state are no longer characteristic of these

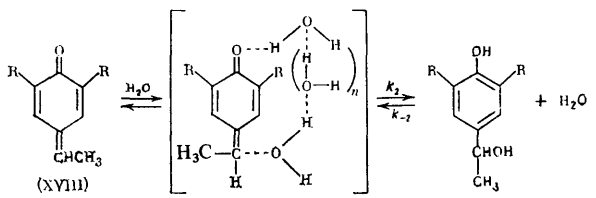
compounds but they retain a high reactivity in reactions with both proton-containing and nucleophilic agents. The effect of the pH of the medium on the mechanism of the 1,6-heteroaddition in reactions of α-alkyl-2,6-di-t-butylmethylenequinones with water is manifested more clearly than in the analogous reaction with the methylenequinone (I) or (II). The following mechanism operates in acid media (pH 2.4 – 5.1):[119]



(XVIII)



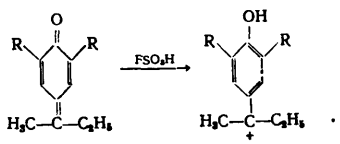
The reaction involving the addition of water to 2.6-di-t-butyl-α-methyl methylenequinone (XVIII) is reversible and the H_2O/D_2O isotope effect is 1.2 in an acid medium. In neutral media (pH 5.1 to 9.5) the transition state incorporates several water molecules and the reaction itself proceeds via the mechanism[119]



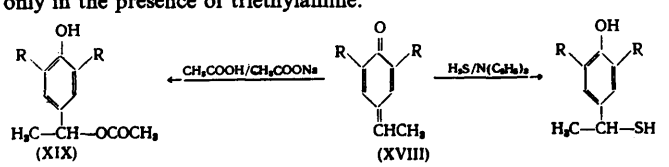
(XVIII)

The H_2O/D_2O isotope effect is 2.56.

The features of the behaviour of the methylenequinone (XVIII) in acid and neutral media examined are general and have been confirmed by other reactions of different α-alkyl- and αα-dialkyl-2,6-t-butylmethylenequinones with alcohols[120] and organic and inorganic acids.[121-124] The formation of the corresponding carbonium ion has been demonstrated by ^1H NMR in the reaction of 2,6-di-t-butyl-α-ethyl-α-methylmethylenequinone with fluorosulphonic acid at -40 °C:[125]

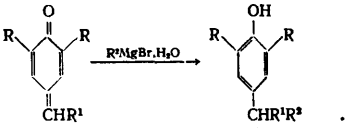


It is noteworthy that the appearance of carbonium ions in the reaction of α-alkylmethylenequinones with proton-containing reagents promotes the irreversible isomerisation of the methylenequinone structure to the aromatic structure of a vinylphenol (see below). The selectivity of many reactions with participation of α-alkylmethylenequinones therefore depends on the specific conditions and increases sharply with increase in the nucleophilicity of the reagent. For example, in the reaction of the methylenequinone (XVIII) with acetic acid, the corresponding 1,6-adduct—3,5-di-t-butyl-4-hydroxy-α-methyl benzyl acetate (XIX)—was obtained in 35% yield, while in the presence of sodium acetate the same reaction takes place more selectively and the yield of compound (XIX) is 90%. The methylenequinone (XVIII) reacts with hydrogen sulphide only in the presence of triethylamine:[30]



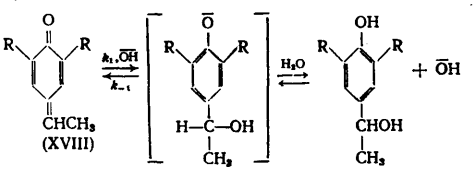
(XIX) (XVIII)

The mode of reaction of methylenequinone homologues with nucleophiles is associated primarily with the characteristic features of the initial step in the interaction of the reagent with the electrophilic centre of the methylene quinone molecule and the character of the decomposition of the intermediate complex formed under these conditions. The reaction of α-alkyl-2,6-t-butyl methylenequinones with amines affords high yields of the corresponding derivatives of *p*-hydroxybenzylamines.[126,127] Organomagnesium compounds also add to the 1,6-positions of the conjugated methylenequinone system with formation of 2,4,6-trialkylphenols; this method has found an application in the synthesis of alkylphenols containing a branched alkyl group in the *para*-position which are difficult to obtain otherwise:[128]



The mechanism of this reaction has not been studied in detail but one can assume that in this instance the addition of the organomagnesium compound takes place synchronously.

In the reaction of the methylenequinone (XVIII) with hydroxide ion (pH 12.3 – 14), 2,6-di-t-butyl-4-vinylphenol is obtained simultaneously with 3,5-di-t-butyl-4-hydroxy-α-methylbenzyl alcohol. The reaction involving the addition of the hydroxide ion to the compound (XVIII) is reversible:[119]



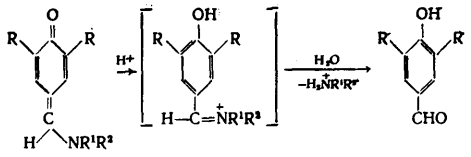
(XVIII)

The rate of the 1,6-addition of water to compound (XVIII) depends on the pH of the medium and is approximately 20 times faster at pH 12.4 – 14 than in neutral media. The reactivity of αα-dialkylmethylenequinones is significantly lower than that of α-alkylmethylenequinones, which is apparently associated with steric factors hindering the attack by the reagent on the electrophilic centre of the methylenequinone molecule.

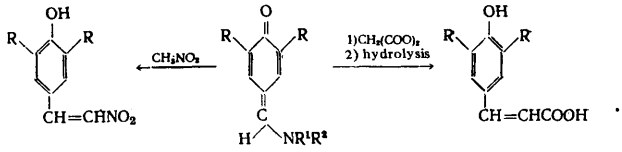
2. Methylenequinones with α-Functional Group Substituents

The electronegative properties of the α-substituent and its capacity to become conjugated with the π-system of the molecule affect directly the reactivity of methylenequinones and this influence is shown most clearly in methylenequinones with α-functional group substituents. Under the influence of the electronic effects of the substituent in the methylene group, the reactivity of the electrophilic and nucleophilic centres of the molecule can alter sharply, which leads in its turn to a change in the behaviour of different α-substituted methylenequinones in the reaction with the same reagent. In the general case in acid media, a proton adding to the carbonyl oxygen atom can induce a bond redistribution with formation of an aromatic system. Naturally, the proton-accepting possibilities of the carbonyl group, which determine the reactivity of methylenequinones in reactions with electrophiles, depend on the degree of conjugation of the π-bond system of the methylenequinone with the α-substituent. αα-(*NN*-dialkylamino)methylenequinones react most readily with acids. The presence of the amino-group in the α-position not only increases the reactivity of the carbonyl group as a result of the high polarisability of the molecule (λ_{max} = 380 nm) but also promotes the aromatisation of the system as a whole by virtue of the possibility of the formation of the azomethine bond system in the transition state. For this reason, αα-(*NN*-dialkylamino)methylene-

quinones are capable of reacting with weak acid reagents, although their reactions in an aqueous medium terminate with the formation of the corresponding *p*-hydroxybenzaldehydes:[30]

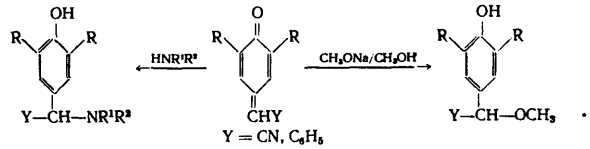


In non-aqueous media, α-(*NN*-dialkylamino)-2,6-di-t-butyl methylenequinones behave as effective *C*-alkylating agents. For example, they react with nitromethane and malonic acid:[30]



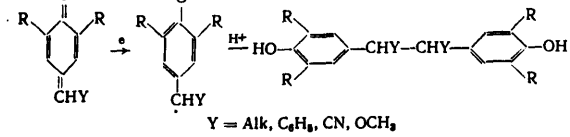
α-Alkoxymethylenequinones behave analogously in the presence of acid reagents. By virtue of the lower nucleophilicity of the oxygen atom at the carbonyl group, α-alkoxymethylenequinones interact only with inorganic or carboxylic acids and do not react with nitromethane, but they do react vigorously with alcohols, amines, and alkalis.[30]

Electron-accepting substituents in the α-position (Y = C_6H_5, COOR, or CN) stabilise the quinonoid bond system of the methylenequinone and the reactions of such methylenequinones with acids beome less typical. However, their reactions with nucleophiles proceed fairly readily with formation of phenolic compounds:[30,69,129]



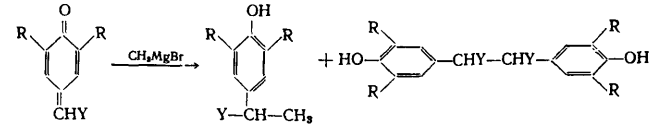
Consequently, in methylenequinones of this kind the carbon atom of the methylene group is fairly reactive with respect to nucleophilic attack.

The most general and typical property of methylenequinones is their ability to participate in oxidation-reduction reactions: a classical example is electrochemical reduction.[108,130,131] The characteristic features of the polarographic reduction of methylenequinones are similar to those of the reduction of quinones. The first polarographic wave of α-substituted 2,6-di-t-butyl methylenequinones in aprotic solvents corresponds to the reversible one-electron reduction, $E'_{1/2}$ depending mainly on the nature of the α-substituent. The main contribution of the electronic effects due to the α-substituent on $E'_{1/2}$ is achieved via the inductive mechanism.[131] The spin density in the radical-anions formed in the one-electron reduction of α-substituted methylenequinones is localised preferentially at the carbon atom of the methylene unit, which determines their ability to undergo spontaneous dimerisation reactions:[102,130]



The dimerisation also occurs under the conditions of the polarographic reduction of α-substituted methylenequinones at a concentration of 10^{-4} M in connection with the high reactivity of the radical-anions produced.

In certain chemical reactions of α-substituted methylenequinones containing electron-accepting substituents, oxidation-reduction processes also take place. For example, the reaction of 2,6-di-t-butyl-α-phenyl- or 2,6-di-t-butyl-α-cyano-methylenequinones with Grignard reagents results in the formation of the corresponding dimers as well as products of the 1,6-addition to the double bond:[56,69]

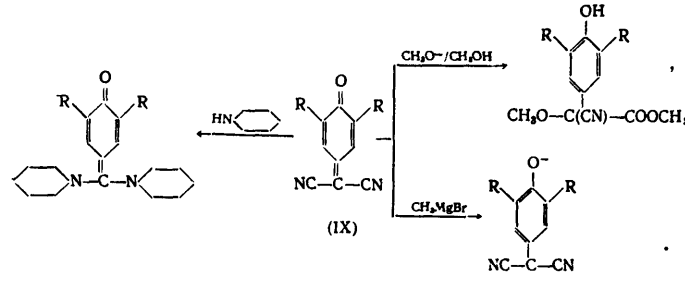


Thus, in the interaction of strong nucleophiles with methylenequinones, a one-electron transfer can take place simultaneously with the main nucleophilic addition reaction.

3. αα-Disubstituted Methylenequinones

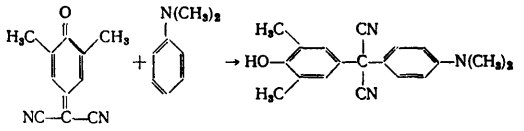
The differences between the properties, chemical behaviour and reactivity of αα-disubstituted methylenequinones containing substituents of different nature are expressed more clearly than for the mono-α-substituted derivatives. In this case, the nature of the functional groups of substituents, their electronegativity, and their capacity for conjugation cause a more marked alteration of the properties characteristic of the unsubstituted methylenequinone and its homologues and new specific properties, characteristic only of the methylenequinones αα-disubstituted by functional groups, appear under these conditions. The fundamental difference in the chemical behaviour of such methylenequinones follows also from the analysis of their physicochemical properties (see above). Thus, on the basis of UV and IR spectroscopic data alone, one can conclude that the "amide" conjugation is so pronounced in αα-(*NN*-dialkylamino)-2,6-di-t-butylmethylenequinones that they virtually lose the properties characteristic of the structure of the mono-α-substituted methylenequinones and that they should be regarded as compounds having a zwitter-ionic structure. These compounds hardly dissolve in organic solvents and are characterised by a high melting point and a high dipole moment (10.8 D).[24]

On the other hand, the quinonoid bond system becomes stable in methylenequinones with electronegative substituents. Such methylenequinones are inert in relation to protic acids and only reactions with nucleophiles become characteristic of them. For example, compound (IX) exhibits very pronounced electron-accepting properties and is capable of forming donor–acceptor complexes with amines and alkoxides. The interaction of the methylenequinone (IX) with a Grignard reagent results in the appearance of a stable radical-anion.[69] The final product of the reaction of the methylenequinone (IX) with piperidine is 2,6-di-t-butyl-αα-dipiperidinomethylenequinone, while its reaction with sodium methoxide leads to the formation of the product of the addition of methanol with partial alcoholysis of one of the nitrile groups:[56]



2,6-Disubstituted αα-dicyanomethylenequinones are stable in acid media, although 1,6-addition reactions are possible under the influence of nucleophiles. In this sense, data concerning the use of

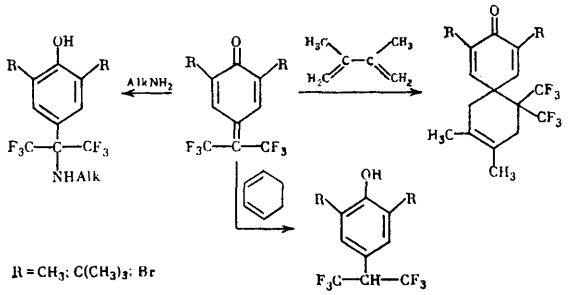
αα-dicyano-2,6-di-methylmethylenequinone as an alkylating agent for dimethylaniline are of definite interest:[18,132]



The majority of αα-disubstituted methylenequinones with electronegative substituents are stable compounds whose stability is almost independent of the presence of substituents in the six-membered ring, which is apparently associated with the sharp decrease of the mobility of the *p*-electrons of the carbonyl group and the consequent loss of capacity for protonation in acid media.

The electron-accepting properties and the electron affinities of αα-diphenylmethylenequinone are almost independent of the character of the substituents in the six-membered ring, their polarographic reduction potentials are similar, and the 1,6-addition reactions take place only under the conditions of base catalysis. For example, the methylenequinone (XIII) does not react with amines and sodium methoxide, but, in the presence of potassium t-butoxide, acetonitrile adds to it.[133,134] 2,6-Dialkyl-αα-diphenylmethylenequinones are capable of forming complexes with phenols and the enthalpy of formation of a hydrogen bond in these complexes increases sharply with decrease in the steric effect generated by the alkyl substituents in the initial methylenequinones.[135]

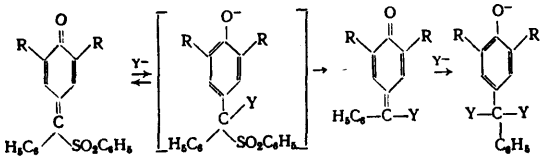
Other examples confirming the similarity of the influence of electronegative α-substituents on the properties of αα-disubstituted methylenequinone are the reactions of 2,6-dialkyl-αα-bis(trifluoromethyl)methylenequinones, which interact with amines and unsaturated compounds but are stable in relation to acids:[136]



R = CH_3; $C(CH_3)_3$; Br

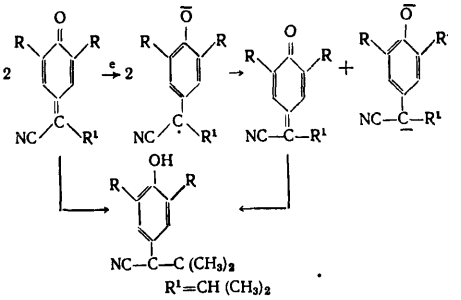
Finally, the reactivity of 2,6-di-t-butyl-α-chloro-α-trifluoromethylmethylenequinone is reduced so much that it has become inert in relation to nucleophiles and is even stable in the presence of alkali metal hydrides.[137]

Reactions leading to the replacement of one of the α-substituents are also characteristic of compounds of the type considered. The characteristic features of the substitution reactions involving αα-disubstituted methylenequinones depend on the thermodynamic stability of the intermediate phenoxide ion and on the strength of the bonds between the α-substituents and the carbon atpm of the methylene unit. An example of such reactions is provided by the substitution of a α-benzenesulphonyl group when 2,6-di-t-butyl-α-phenyl-α-benzenesulphonylmethylenequinone is acted upon by nucleophiles:[138]



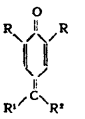
Reactions of this type, involving nucleophilic substitution and subsequent addition, have been investigated under conditions where the above methylenequinone was acted upon by alkalis, alkoxides, thiophenoxides, and cyanides. The method has found an application in the synthesis of derivatives of sterically hindered phenols which are otherwise difficult to obtain.

Quantitative data characterising the influence of α-substituents of different nature on the reactivity of αα-disubstituted 2,6-di-t-butylmethylene quinones in the reaction with the simplest nucleophile (the electron) have been obtained as a result of polarographic measurements and electrochemical studies (Table 4). In this series, the greatest electron affinity is shown by the methylenequinone (IX), whose electrochemical reduction takes place in two stages, a stable radical-anion being formed at the potential of the first polarographic wave $E'_{1/2}$. This method makes it possible to estimate the reactivity of methylenequinones containing in the α-positions simultaneously electron-accepting and electron-donating substituents. Furthermore, it has been possible to establish the characteristic features of the electrochemical reduction of 2,6-di-t-butyl-α-cyano-α-isopropyl methylenequinone associated with the phenomena involving the disproportionation of the intermediate radical-anion and the isomerisation of the initial methylenequinone to vinylphenol under electrochemical reduction conditions:[56]



The EPR spectrum of the radical-anion has been recorded in the course of the reduction of 2,6-di-t-butyl-α-cyano-α-isopropylmethylenequinone by metallic potassium in tetrahydrofuran.[56]

Table 4. The half-wave potentials (relative to the saturated calomel electrode) for the polarographic reduction of αα-disubstituted 2,6-di-t-butyl methylenequinones (in dimethylformamide with tetrabutylammonium perchlorate as the supporting electrolyte).[56]

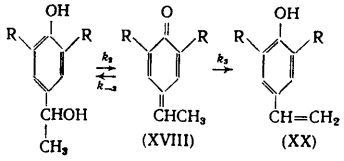


R^1	R^2	$E'_{1/2}$, mV	$E''_{1/2}$, mV	R^1	R^2	$E'_{1/2}$, mV	$E''_{1/2}$, mV
CH_3	CH_3	1370	—	CH_3	CN	750	1480
C_6H_5	C_6H_5	570	1130	C_2H_5	CN	770	1490
CN	CN	120	990	$CH(CH_3)_2$	CN	780	1500
NC_5H_{10}	NC_5H_{10}	2125	2275	C_6H_5	CN	570	1130
C_6H_5	NC_5H_{10}	1516	—	NC_5H_{10}	CN	949	1544

VI. ISOMERISATION OF METHYLENEQUINONES

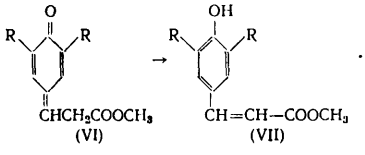
The high reactivity of methylenequinones is associated with thermodynamic factors and the possibility of a rearrangement of the bond system of the methylenequinone to the aromatic bond system of a phenol. This possibility is manifested clearly in the isomerisation of methylenequinone homologues to vinylphenols. The isomerisation of alkylmethylenequinones to vinylphenols is irreversible,

so that many reactions of the methylenequinones are accompanied by the formation of vinylphenol derivatives. Thus in an aqueous medium at pH 8.2 the isomerisation of the methylenequinone (XVIII) to 2,6-di-t-butyl-4-vinylphenol (XX) takes place simultaneously with its hydration, both reactions proceeding at similar rates under the conditions indicated (k_2/k_3 = 2.8):[119]



(XVIII) (XX)

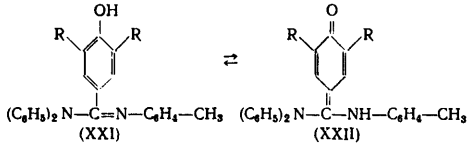
In acid or alkaline media, the rate of the 1,6-addition reaction is significantly higher than the rate of isomerisation, but, with increase in the reaction time, the yield of the phenol (XX) increases because of the irreversibility of the isomerisation stage. At 70–75 °C the irreversible isomerisation of α-alkylmethylenequinones takes place in the presence of alumina.[139] Vinylphenols are obtained in substitution reactions with participation of benzyl derivatives of phenol. Many of these reactions proceed via a stage involving the formation of the corresponding methylenequinones, whose isomerisation actually leads to the vinylphenols.[140,141] The functional-group substituents in the α-position promote the isomerisation of methylenequinone to vinylphenol, the process actually occurring spontaneously at room temperature, for example:[56]



(VI) (VII)

The pure methylenequinone (VI) rearranges quantitatively to a cinnamic acid derivative after two days at 20 °C.

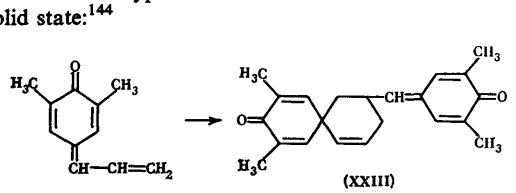
Under the influence of functional-group substituents in the α-position, the thermodynamic stability of the methylenequinone structure increases and tautomeric transformations are observed in the case of α-aminomethylenequinones.[142] For example, the prototropism of 3,5-di-t-butyl-4-hydroxy-*NN*-diphenyl-*N'*-tolybenzamidine (XXI) is observed in solution and leads to the establishment of thermodynamic equilibrium with the corresponding αα-diaminomethylenequinone (XXII):



(XXI) (XXII)

Both tautomers, (XXI) and (XXII), have been isolated in a pure state. At 25 °C, the ratio of compunds (XXI) and (XXII) is 42 : 58, $\Delta G^{\ddagger}_{298}$ = 70.8 kJ mole^{-1}, and $\Delta S^{\ddagger}$ = −16.4 e.u. The solvent polarity affects the ratio of the tautomers in solution and hence the nature of the solvent is one of the factors influencing the stability of the methylenequinone bond system.[143]

Methylenequinones containing vinyl substituents in the α-position undergo Diels-Alder-type dimerisations in concentrated solutions or in the solid state:[144]



(XXIII)

The cyclohexadiene structure is retained in reactions of this type and a methylenequinone (XXIII) derivative having a more complex structure is formed. The dimerisation reaction is irreversible.

—o0o—

The interest in the chemistry of methylenequinones has not weakened for a long time. In our day, they remain convenient objects for the investigation of various aspects of theoretical and synthetic organic chemistry and photochemistry and also for the study of the pathways leading to the biogenesis of natural products.

The structure of methylenequinones is labile, which is the reason for their high reactivity. Both homolytic and heterolytic reactions are characteristic of them. Being vinylogues of ketones, methylenequinones possess also many of their properties, but these are manifested more strikingly and are more varied.

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