23. N.M.Milyaeva, Zhur.Neorg.Khim., 3, 2011 (1958).
24. M.J.Jorgenson and D.R.Hartter, J.Amer.Chem.Soc., 85, 878 (1963).
25. J.C.D.Brand, J.Chem.Soc., 997 (1950).
26. J.C.D.Brand, W.C.Horning, and M.B.Thornely, J.Chem. Soc., 1374 (1952).
27. L.P.Hammett and M.A.Paul, J.Amer.Chem.Soc., 56, 827 (1934).
28. A.I.Gel'bshtein, G.G.Shcheglova, and M.I.Temkin, Zhur. Neorg.Khim., 1, 282 (1956).
29. R.P.Bell, A.L.Downing, and J.A.Noble, J.Chem.Soc., 3106 (1955).
30. M.I.Vinnik, R.N.Kruglov, and N.M.Chirkov, Zhur.Fiz. Khim., 30, 827 (1956).
31. T.G.Bonner and J.C.Lockhart, J.Chem.Soc., 2840 (1957).
32. K.Yates and H.Wai, J.Amer.Chem.Soc., 86, 5408 (1964).
33. E.Heilbronner and S.Weber, Helv.Chim.Acta, 32, 1513 (1949).
34. M.I.Vinnik, Candidate's Thesis, Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow, 1953.
35. "Inorganic Syntheses" (Edited by L.F.Audrieth), McGraw-Hill, New York, 1950, Vol.3, p.85.
36. R.P.Bell, K.N.Bascombe, and I.C.McConbrey, J.Chem. Soc., 1286 (1956).
37. H.H.Hyman, M.Kilpatrick, and I.I.Katz, J.Amer.Chem. Soc., 79, 3668 (1957).
38. E.Högfeldt and J.Bigeleisen, J.Amer.Chem.Soc., 82, 15 (1960).
39. S.J.Bass, R.H.Flowers, R.J.Gillespie, E.A.Robinson, and C.Solomons, J.Chem.Soc., 4315 (1960).
40. T.S.Karetnikov, Zhur.Fiz.Khim., 28, 1331 (1954).
41. L.Ochs, I.Gueron, and M.Magat, J.Phys.Radium, 1, 85 (1940).
42. H.S.Gutowsky and A.Saika, J.Chem.Phys., 21, 1688 (1953).
43. C.C.Hood, O.Redlich, and C.A.Reily, J.Chem.Phys., 22, 2067 (1954).
44. T.F.Young, L.F.Maranville, and H.M.Smith, in "The Structure of Electrolyte Solutions" (Edited by W.J.Hamer), Wiley, New York, 1959.
45. R.H.Boyd, J.Amer.Chem.Soc., 85, 1555 (1963).
46. N.T.Librovich and M.I.Vinnik, Dokl.Akad.Nauk SSSR, 166, 647 (1966).
47. L.P.Hammett and R.P.Chapman, J.Amer.Chem.Soc., 56, 1282 (1934).
48. T.G.Bonner and J.C.Lockhart, J.Chem.Soc., 364 (1957).
49. N.A.Izmailov and Yu.F.Rybkin, Dopovidi Akad.Nauk Ukrain.RSR, 69, 1071 (1962).
50. R.H.Boyd, J.Phys.Chem., 67, 737 (1963).
51. N.C.Deno, H.J.Peterson, and E.Saeber, J.Phys.Chem., 65, 199 (1961).
52. Yu.F.Rybkin and N.F.Shevchenko, Elektrokhimiya, 1, 46 (1965).
53. B.Gutbezahl and E.Grunwald, J.Amer.Chem.Soc., 75, 559 (1953).
54. Yu.V.Moiseev and M.I.Vinnik, Zhur.Strukt.Khim., 4, 336 (1963).
55. H.S.Harned and B.B.Owen, "Physical Chemistry of Electrolytic Solutions" (Translated into Russian), Inostr.Lit., Moscow, 1952.
56. R.A.Robinson and R.H.Stokes, "Electrolyte Solutions" (Translated into Russian), Inostr.Lit., Moscow, 1963.
57. W.F.Giaque, E.W.Hornung, J.E.Kunzler, and T.R.Rubin, J.Amer.Chem.Soc., 82, 62 (1960).
58. Landolt-Börnstein, "Physikalisch-chemische Tabellen", Springer, Berlin, 1936, 3.Ergänzungsband.
59. K.N.Bascombe and R.P.Bell, Discuss.Faraday Soc., No.24, 158 (1957).
60. P.A.H.Wyatt, Discuss.Faraday Soc., No.24, 163 (1957).
61. E.Högfeldt, Acta Chem.Scand., 14, 1627 (1960).
62. K.L.Elmore, C.M.Mason, and I.H.Christensen, J.Amer. Chem.Soc., 68, 2528 (1946).
63. S.G.Entelis and N.M.Chirkov, Zhur.Fiz.Khim., 31, 1311 (1957).
64. N.C.Deno and R.W.Taft, J.Amer.Chem.Soc., 76, 244 (1954).
65. N.G.Zarakhani and M.I.Vinnik, Zhur.Fiz.Khim., 36, 916 (1962) [Russ.J.Phys.Chem., 483 (1962)].

Institute of Chemical Physics,
Academy of Sciences of the
USSR, Moscow

U.D.C. 547.565:541.623

TAUTOMERIC TRANSFORMATIONS OF PHENOLS

V. V. Ershov and G. A. Nikiforov

CONTENTS

1. Introduction 817
2. Tautomerism of phenols 818
3. Tautomerism of nitrosophenols 823
4. Tautomerism of azophenols 825
5. Equilibrium phenol–quinonoid transformations of *p*-substituted phenols 827

1. INTRODUCTION

Problems of the tautomerism of organic compounds are at present of interest to many research workers[1]. Even in the most familiar type of tautomerism (keto–enol tautomerism) there are little-studied relationships and phenomena, in particular the tautomerism of phenolic compounds. These transformations aroused the interest of research workers at an early date, but the systematic study of this interesting phenomenon was made possible only by the development of modern physical methods for studying organic compounds.

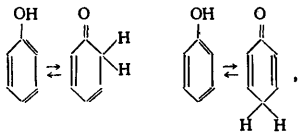
In keto–enol tautomeric transformations of organic compounds, the tautomerism of hydroxyaromatic compounds occupies a special place, since the phenomenon is accompanied by breakdown of the aromatic bond system. The present paper summarises results concerning the actual phenomenon of tautomerism in the phenol series, and also some reactions of substituted phenols (for example, salt formation), as a result of which equilibrium is established between the aromatic (phenolic) and quinonoid or quinolide†

† We apply the term "quinolide", as distinct from "quinonoid" in the description of bond systems, to cyclohexadienones in which the carbon atom in the *ortho*- or *para*-position relative to the carbonyl group is joined by ordinary (not double) bonds to two substituents.

(cyclohexadienone) bond systems. This review does not deal with the reactions of phenols in which substances with a quinolide structure are obtained merely as intermediates or are formed irreversibly by the action of electrophilic and radical reagents on substituted phenols. Reactions of the last type (phenol–dienone bond rearrangement) were reviewed in detail earlier[2]. Since we shall restrict ourselves to the regular features of equilibrium transformations in the phenol series, we shall naturally not consider processes associated with the phenomenon of mesomerism in phenolic compounds, since this is of independent interest.

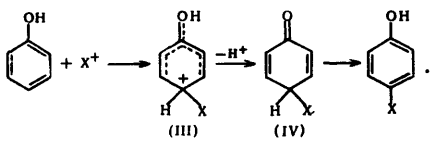
2. TAUTOMERISM OF PHENOLS

The possibility of tautomeric transformation of phenols into compounds with an *ortho*- or *para*-quinolide bond system (cyclohexadienones)



(I) (II)

is usually regarded[3,4] as a specific case of keto–enol tautomerism. Support for this view is provided by certain features which the phenomena have in common. A phenol molecule containing a hydroxyl group and a bond of aromatic type (with electron content very close to that of a double bond) should be converted into an alicyclic carbonyl compound. In reality, however, this does not take place in the simplest phenols, since the equilibrium is displaced completely towards the phenolic (enol) form. This is in fact the chief characteristic of the phenol ⇌ cyclohexadienone tautomerism which we are considering. Moreover, if it is assumed that the conversion of phenol into the cyclohexadienone with the *para*-quinolide structure (II) is energetically more favourable, phenol–dienone tautomerism, unlike keto–enol tautomerism, will not have the characteristic of a triad tautomeric transformation. Thus its mechanism should differ slightly from that of ordinary keto–enol tautomerism. Unfortunately, the question of the mechanism of phenol–dienone tautomerism remains open. Its mechanism should apparently be close to that of electrophilic substitution, which in the phenol series has characteristic features[5] associated with the intermediate formation of dienone systems of types (I) or (II). According to the mechanism at present accepted for electrophilic substitution in the phenol series (see for example Nenitzescu[6]) the first stage in the substitution is the formation of the benzonium ion (III), which is readily stabilised by the removal of a proton from the hydroxyl group with the formation of an intermediate neutral quinolide compound (IV), which rapidly isomerises into a substituted phenol. Thus for most monohydric phenols the formation of cyclohexadienone structures is possible only at the moment of reaction under the influence of an electrophilic reagent‡:

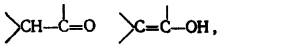


(III) (IV)

‡ See the earlier review[2] for more details.

Obviously, if it is assumed that X = H, we shall be dealing with the typical keto–enol tautomerism of phenol itself. Analogous considerations can be applied to the *ortho*-quinolide tautomer. In these transformations, however, the exact mechanism of the transformation of the dienone (IV) into the phenol has not been studied; this is directly related to the tautomerism of phenols. The question of the mechanism of phenol–dienone tautomerism is of considerable practical importance, since examples[7-9] have been described (without reference to mechanism) of the irreversible transformation of certain *para*-quinolide compounds of type (IV) into the corresponding phenols§. Moreover, even where phenol–dienone tautomerism is possible (for example, anthrol ⇌ anthrone) almost no discussion of the mechanism of these transformations has been published.

Thus all the characteristic features of phenol–dienone tautomerism are related to the extreme stability of the phenolic (enol) form. This stability is extremely regular, despite the fact that comparison of the two bond systems



shows that the formation of the carbonyl group is energetically much more favourable (by 18.6 kcal mole^{-1})[11] than that of the enol group. The possibility of partial enolisation arises, however, even in acetoacetic ester, chiefly as a result of the gain in the energy of delocalisation with another carbonyl group. In the phenol–cyclohexadienone system which we are considering, however, the gain in resonance energy (the energy of aromatic delocalisation, which for benzene amounts to ~ 36 kcal mole^{-1} [12,13]) is much greater than the energy required for enolisation of the carbonyl group, so that the aromatic bond system becomes the most favoured. Thus the simplest phenols exist in only one form and there is no possibility of tautomerism in these compounds. This conclusion is confirmed by all the chemical and physical properties of the simplest phenols. It thus becomes evident that the manifestation of phenol–dienone tautomerism is possible only when there are additional factors leading in some way to a decrease in the difference between the energies of enolisation and aromatic conjugation. The most important such factors are the following.

1. Increase in the number of hydroxyl groups in the aromatic nucleus. Here tautomerism is possible because the energy of aromatic delocalisation must compensate the energy of enolisation of not one but several carbonyl groups.

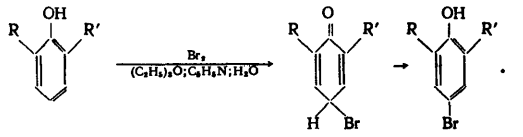
2. Formation of phenoxide ions. In the equilibrium transformation involving a phenoxide anion there is no need to expend energy on the removal of a proton, and this naturally makes the equilibrium system more labile. Moreover, the fact that the aromatic ring is always involved in the redistribution of the negative charge in the phenoxide ion should facilitate to a considerable extent the production of the carbonyl form.

§ Recently, de la Mare in a private communication[10] suggested that under the conditions of acid or base catalysis the transformation of the dienone (IV) into the substituted phenol involves initially the attachment of a proton from the solvent to the carbonyl oxygen of the dienone, followed by the removal of a proton from the *gem*-position. The mechanism may be different, however, in a spontaneous transformation.

3. Decrease in the energy of aromatic delocalisation in the phenol ring as a result of its condensation with other aromatic systems.

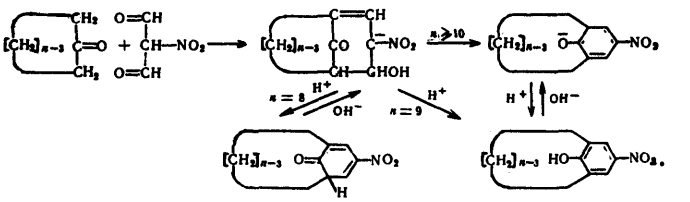
4. The introduction, into the *ortho*- or *para*-position of the phenol, of groups exhibiting a marked negative conjugation effect. Here a decrease in the energy of aromatic delocalisation takes place as a result of conjugation of the ring with the group under consideration; this may lead to a redistribution of the electron density in the molecule with the formation of a quinonoid (but not quinolide) bond system. This leads to the possibility of a slightly different tautomeric transformation of the phenol molecule, in which an electronegative group takes part in the transfer of a proton from the phenolic hydroxyl (for example, the tautomerism of nitrosophenols).

Tautomerism in phenolic compounds arises most readily when a phenolic aromatic ring is influenced simultaneously by several of the above factors. Here, the tautomerism conditions (influence of temperature and the medium) and steric phenomena are naturally of considerable importance. In the tautomerism of phenols the spatial factor (as in classical keto–enol tautomerism [14]) leads to an increase in the stability of the keto-form and retards its rearrangement into the phenol. A similar influence is shown to some extent by the steric factor even in mononuclear polyhydric phenols. For example, in the bromination of 2,6-dialkylphenols in the presence of substances exhibiting proton-accepting properties, bromo-*p*-quinolide compounds were isolated in the individual state; these isomerised spontaneously into the corresponding *p*-bromophenols [7,8]:



The lifetime of these quinolide compounds depends to a significant extent on the steric hindrance around the carbonyl group, and at 20° amounts to ten days for R = R′ = $C(CH_3)_3$, or 4 h for R = R′ = $CH(CH_3)_2$; for R = R′ = CH_3 the bromoquinolide compounds exist only in dilute solutions and isomerise instantly into the bromophenol when attempts are made to isolate them. Stabilisation of a cyclohexadienone structure as a result of screening of the carbonyl group by t-butyl groups was also described by Kharasch [9], who by the recombination of 2,6-di-t-butylphenoxyl radicals obtained a bis-*p*-quinolide compound which readily isomerised into 3,3′,5,5′-tetra-t-butyl-4,4′-dihydroxybiphenyl.

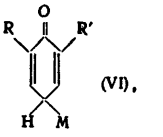
Prelog [15,16] described another type of steric influence on the stability of a cyclohexadienone having a hydrogen atom as one of the *gem*-substituents. By condensing cyclononanone with nitromalonic aldehyde followed by acidification of the reaction mixture, he obtained the dicyclic dienone (V), which is an isomeric keto-form of the corresponding nitrophenol. The dienone (V) is extremely stable and isomerisation into the phenol is prevented by the rigidity of the structure, which does not allow the formation of a double (or in this example aromatic) bond at the head of the dicyclic bridge, in accordance with Bredt's rule [17]. When the cyclic ketone is enlarged by one methylene group, however, the condensation product is converted into the nitrophenol on analogous treatment, and with further increase in the dimensions of the ring the anion of the corresponding phenol is obtained immediately in the reaction mixture:



(V)

While dealing with stabilisation of the carbonyl form by the steric factor, we should point out that for a prolonged period one could find in the literature the unrefuted opinion, put forward in 1911 by Mayer [18], that tautomerism was possible in 3,4-di-t-butylphenol because of the marked steric hindrance in the *o*-di-t-butylbenzene system [19]. This phenol was prepared in 1964, however, and it was shown to exist only in the usual phenolic form [20].

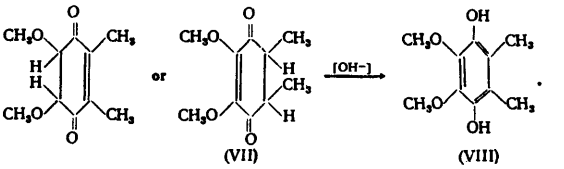
The influence of the steric effect is also seen in the formation of salts by phenols showing steric hindrance¶; some authors [21,22] on the basis of the chemical properties, have assigned the quinolide structure (VI) to these compounds in the solid state. In solution, these metal derivatives have been assigned [23,24] the structure of a levelled (ambident) ion. Treatment of these solutions with alkyl halides leads to the attachment of the alkyl residue to the phenol in the *para*-position. The quantity of C-isomer depends on the steric hindrance created by the *ortho*-alkyl groups and the magnitude of the entering alkyl group:



(VI),

where M = K, Na, or Li. Analogous reactions with these salts are undergone by benzoyl chloride [25], acrylonitrile [22,25], ethylene oxide [21], and a number of other compounds [21].

As already noted, increase in the number of hydroxyl groups in the aromatic nucleus, as a result of a decrease in the difference between the stabilisation energies of the keto- and enol forms [26], should favour tautomerism and this should be reflected in the properties and reactivity of polyhydric phenols. The individual existence of the keto-form should then be possible even when the influence of the steric effect is smaller. For example, the antibiotic gliorosein (VII), according to chemical and spectroscopic data, is an isomeric keto-form of the corresponding substituted hydroquinone (VIII), into which it can be readily converted in the presence of basic substances [27]:

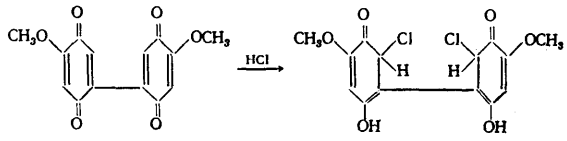


(VII) (VIII)

The formation of a similar diketo-form was also observed in the addition of hydrogen bromide to 2,6-dimethoxyquinone [28]. An analogous ketone (IX) was also obtained [29,30] in

¶ In 2,6-di-t-alkylphenols the screening of the phenolic hydroxyl is so great that these phenols do not dissolve in alcoholic solutions of alkalis and do not form salts under ordinary conditions. Salts of these phenols can be formed only by treating them with alkali metals in benzene or liquid ammonia.

the biphenyl series by the addition of hydrogen chloride to the diquinone (X). This ketone could not be enolised, however, since on recrystallisation it decomposes to the original components:



(X) (IX)

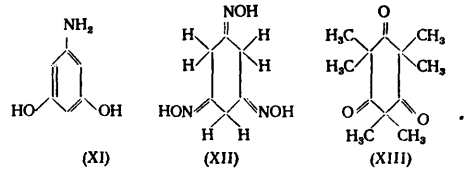
Here we see a general property of the keto-forms of substituted hydroquinones, whose stabilisation into quinonoid compounds with the removal of a molecule of an inorganic substance takes place more readily than the transformation into isomeric hydroquinones. This characteristic has been most extensively studied for compounds of the naphthalene series (see p. 823).

A large amount of material on the chemical properties and reactivity of polyhydric phenols indicates the possibility that many of these compounds react in a tautomeric keto-form. Thus resorcinol, like $\alpha\beta$-dicarbonyl compounds, is readily reduced by sodium amalgam to cyclohexane-1,3-dione[31].

The behaviour of phenols, containing different numbers of hydroxyl groups, in their reactions with ammonia is also characteristic. The replacement of the phenolic hydroxyl group in a monohydric phenol by an amino-group takes place with difficulty and under very severe conditions (350–450°, 50–60 atm), whereas with resorcinol this reaction takes place fairly readily at ~ 200°,[32] and phloroglucinol is converted almost quantitatively into 5-aminoresorcinol (XI) at room temperature in alcoholic ammonia solution[33,34]. These reactions evidently take place by the same mechanism as the action of ammonia on carbonyl compounds capable of undergoing prototropic transformations[35].

Finally, the reaction of phloroglucinol with hydroxylamine is extremely specific. As early as 1886, Bayer[36], in a study of this reaction, isolated a compound to which he assigned the structure of the cyclic trioxime (XII). Much later (1956) the structure of this substance was confirmed by spectroscopic methods[37]. Its infrared spectra show bands corresponding to the absorption of the –C=N group (1653 cm^{-1}), and the ultraviolet spectrum does not contain the maximum due to aromatic absorption.

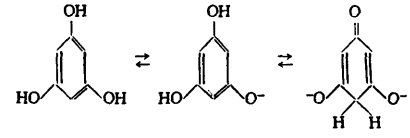
Unusual behaviour is shown by phloroglucinol and resorcinol[38-45] on alkylation by alkyl halides in aqueous alkali. Thus methylation by methyl iodide in the presence of potassium hydroxide gives a mixture of *O*- and *C*-methyl derivatives, and with an excess of methyl iodide the hexamethyl derivative (XIII) can be obtained from phloroglucinol[40-44,46-48]. A more detailed study[49] of this reaction for the example of 2,4,6-trihydroxyacetophenone showed that the composition of the mixture of final products depends to a marked extent on the concentration of alkali in the solution. This reaction resembles the alkylation of metallic derivatives of acetoacetic ester. Chlorination[50,51] and bromination[52,53] of phloroglucinol with an excess of halogenating agent also gives analogous hexahalogeno-derivatives:



(XI) (XII) (XIII)

On the other hand, there are reactions in which phloroglucinol behaves as a typical phenol: it gives the triacetate with acetyl chloride, and it is methylated by diazomethane with the formation of the trimethyl ether[54,55].

Thus the chemical properties of polyhydric phenols, in particular phloroglucinol, indicate that the compounds may react in both the keto- and enol forms. Tautomerism in phloroglucinol has not been observed directly, however. The Raman[56], ultraviolet, and infrared[37] spectra indicate that phloroglucinol consists exclusively of trihydroxybenzene both in solution and in the solid state. Naturally, here it might be assumed that phloroglucinol contains in equilibrium extremely small quantities of the keto-form, which are not detected by the methods used. It is more probable, however, that the dual reactivity of phloroglucinol is due to the tautomeric transformation of its anion, since all the reactions confirming the existence of the keto-form of phloroglucinol generally take place in the presence of bases. The existence of the phloroglucinyl oxide anion in the tautomeric keto-form can now be taken as proved, so that the question of the tautomerism of phloroglucinol reduces to the tautomerism of its anion; the most stable keto-form should be the doubly-charged phloroglucinyl oxide anion:



According to a number of authors[57-61], evidence for this is provided by the appearance of a maximum in the 250 nm region, characteristic of *para*-quinolide compounds, in the ultraviolet spectrum of an alkaline solution of phloroglucinol. Formation of this structure is also indicated by the sharp increase in the second dissociation constant of phloroglucinol compared with other polyhydric phenols (Table 1).

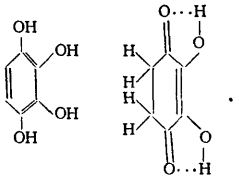
Finally, the existence of the doubly-charged phloroglucinyl oxide anion in the keto-form was proved most convincingly by proton magnetic resonance[63]. The PMR spectrum of aqueous phloroglucinol solution shows a single maximum corresponding to aromatic protons (τ = 3.95), which is displaced slightly when one mole of alkali is added (τ = 3.98). The addition of a second mole, however, produces sharp changes in the spectrum: the maximum due to the aromatic protons disappears, with the production of two new peaks; one of these (τ = 4.97) corresponds to protons associated with an alkene double bond, and the other (τ = = 7.00) corresponds to the protons of a methylene group. The chemical shift of the observed peaks is insensitive to change in concentration and temperature. These observations indicate the existence of a doubly-charged anion in the form of an alicyclic isomer, and according to the infrared

TABLE 1. Dissociation constants of polyhydroxyphenols[62]

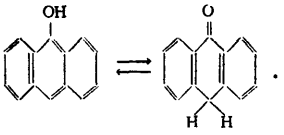
Phenol	$10^9 K_1$	$10^{12} K_2$
Phloroglucinol	3.56	1320.00
Pyrogallol	9.67	2.30
Resorcinol	0.71	4.78
Pyrocatechol	0.75	0.84
Hydroquinone	0.12	0.91

spectra[63] this structure is preserved in the disodium salt of phloroglucinol in the solid state. It thus follows that un-ionised phloroglucinol and singly-charged and doubly--charged ionic forms are present in equilibrium, and pure tautomerism between two forms of the doubly-charged anion is not observed. The formation of the doubly-charged phloroglucinyl oxide anion is apparently accompanied by simultaneous rearrangement of the aromatic bond system into a dienone system; this is extremely characteristic of the ionisation of certain substituted phenols (see p. 828).

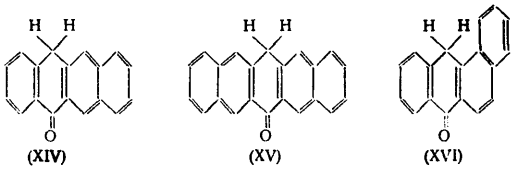
As a result of the introduction of another hydroxyl group into the aromatic ring, 1,2,3,4-tetrahydroxybenzene can exist in two individual isomeric forms[64,65]. Under appropriate conditions the isomers can be converted into one another, but there is no reversible equilibrium between them. Here the stability of the keto-form is influenced not only by the above energetic features, but also by intramolecular hydrogen bonds formed as a result of the favourable mutual arrangement of the hydroxyl and keto-groups (see p. 822).



The above published data indicate that in the mononuclear phenol series (mono-, di-, and poly-hydric), actual tautomerism, as a mobile equilibrium, does not exist. This state of affairs is not preserved, however, on going to the hydroxyl derivatives of polycondensed aromatic systems. Even in naphthols the symmetrical character of the π-electron cloud is disturbed, and this naturally leads to a decrease in the aromaticity of the phenolic ring. Approximate quantum-mechanical calculation shows that the 1–2 bonds of naphthalene are closer to double bonds than the bonds in benzene, and also that the 1,2,3,4-system of naphthalene is similar to some extent to the buta-1,3-diene system and to an even greater extent to the 1,4-diphenylbuta--1,3-diene system[66]. Thus the energy used in enolisation is compensated to a smaller extent by the energy of aromatic delocalisation in the naphthol series than in mononuclear hydroxyaromatic compounds. As a result, in the naphthalene series, even the monohydric hydroxyl derivatives exhibit the properties of the tautomeric keto-form in their chemical reactions. Thus β-naphthol is readily reduced to β-tetralone[67,68], undergoes bromination with the formation of derivatives of the keto-form with *gem*-substituents in the α-position[69], etc. As in phloroglucinol, however, tautomerism is not observed directly in the naphthols. In monohydric phenols tautomerism becomes possible only when the phenol ring is condensed with two aromatic nuclei. Thus in unsubstituted anthracene the energy of aromatic delocalisation is slightly greater than the sum of the energy of conjugation of two isolated aromatic rings[70], but when a hydroxyl group is introduced into the *meso*-position of anthracene, this excess delocalisation energy cannot completely compensate the enolisation energy. As a result, 9-hydroxyanthracene (anthrol) is able to undergo reversible conversion into the corresponding ketone (anthrone) in which the two isolated aromatic rings are conjugated with the carbonyl group, leading to an even greater increase in the stability of the keto-form:



Thus the appearance of tautomerism in a phenolic compound indicates a decrease in the aromaticity of the ring attached to the hydroxyl group. This is readily seen on going from phenol to other monohydroxy-derivatives of polycondensed aromatic compounds. The more extensive the polynuclear aromatic system, the greater the probability of conversion of the enol form into the keto-form, and the greater the stability of the keto-form. Thus the keto-form of hydroxynaphthacene (XIV) shows only a slight tendency to undergo enolisation, and the phenolic form of the pentacenes (XV) is unknown[4]:



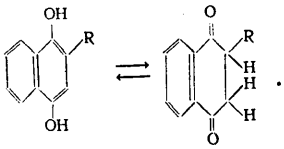
(XIV) (XV) (XVI)

An attempt to bring about the isomerisation of (XV) in the usual way by heating in concentrated sodium hydroxide was unsuccessful. The isomer of hydroxynaphthacene — benzanthrol (XVI) — however, exists in both forms, which can be readily separated[71].

Of the above possible tautomeric transformations, the tautomerism of anthrol has been most studied. This is at present perhaps the simplest monohydroxyaromatic compound for which two isomeric forms are known to exist in equilibrium. As early as 1911, Mayer[18] found that the anthrol–anthrone equilibrium can exist in the absence of catalysts. A more detailed study[72] showed that in alcohol, 9-anthrone is enolised to the extent of only 11.5%. Slow cooling leads to crystallisation of the non-enolised product, but on rapid cooling the mixture contains crystals of 9-anthrol. The two forms are distinguished by their chemical properties. The keto-form shows a relatively low activity in the absence of catalysts bringing about enolisation. Heating in 10% sodium hydroxide for 10 min in a current of nitrogen with subsequent acidification leads to complete enolisation of anthrone. The reverse isomerisation takes place, however, when the resulting 9-anthrol is dissolved in ether, alcohol, or dioxan[73]. Alkylation of 9-anthrone by benzyl chloride in the presence of alkali gives 10,10-dibenzyl-9-anthrone. Hydrolysis of 9-benzyl--10-benzyloxyanthracene by treatment with hydrochloric acid leads to rapid isomerisation of the resulting 10-benzyl--9-anthrol into the corresponding anthrone[74]. Kinetic studies of the isomerisation of anthrol into anthrone showed that this reaction is of first order, the activation energy and rate of isomerisation depending to a marked extent on the solvent[75].

On going to polyhydroxy-derivatives of condensed hydrocarbons, all the above features are shown even more clearly, and the possibility of tautomeric transformations arises in dihydroxynaphthalenes containing both hydroxyl groups in the same ring, particularly if on formation of the keto-form the carbonyl groups are further stabilised by conjugation with the other aromatic ring. These changes were studied in

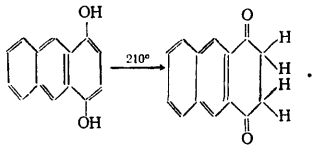
most detail by Thomson[4,76-80]. 1,4-Dihydroxynaphthalene (R = H) and 1,4-dihydroxy-2-methylnaphthalene (R = CH_3) on fusion (~ 200°) form equilibrium mixtures containing 10% of the diketo-forms (XVIII):[76,81,82]



(XVII) (XVIII)

Under ordinary conditions, however, both the dienol (XVII) and the diketone (XVIII) are stable compounds, and equilibrium between them does not exist. According to Braude's data[83], in the titration of the hydroquinone (XVII) with cerium sulphate in petroleum ether solution at 130°, the titre decreases gradually to a definite limit. Tautomeric equilibrium is evidently established under these conditions also. The reverse conversion of the diketone (XVIII) into the dienol (XVII) takes place when the diketone is dissolved in cold alkali and the resulting solution is acidified. Spectroscopic studies[76] showed that under ordinary conditions the diketone (XVIII) undergoes no structural changes in solution or in the solid state.

In the anthracene series the ability of 1,4-dihydroxy--derivatives to undergo conversion into the diketo-form is even greater, and this is naturally associated with a further decrease in the aromaticity of the phenolic ring. Thus on fusion (210°) 1,4-dihydroxyanthracene (XX) is converted in 50% yield into the corresponding 1,2,3,4-tetrahydro-1,4--diketoanthracene (XIX):[78]

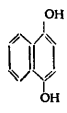
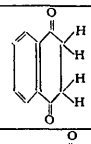
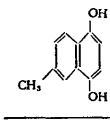
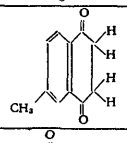
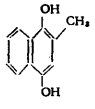
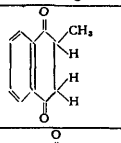
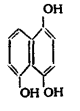
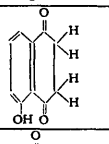
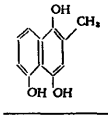
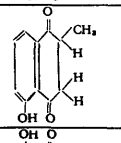
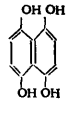
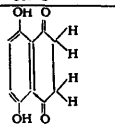


(XX) (XIX)

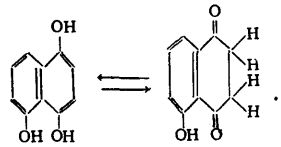
Here the diketone is more stable than the dienol. The diketone can be converted into the dienol by dissolving in dilute alkali. Analogous properties are shown by 1,4-dihydroxy-9,10-diphenylanthracene[84]. The equilibrium 9,10-dihydroxyanthracene–anthraquinol system is also well known[85].

The stability of the diketo-forms of the 1,4-dihydroxy--derivatives of polycondensed compounds which we have considered increases appreciably when hydroxyl groups are introduced into the α-position of a neighbouring aromatic ring. This increased stability is due to the production of an intramolecular hydrogen bond in the keto-form as a result of the favourable spatial arrangement of the hydroxyl and carbonyl groups. In these compounds, the energy of aromatic delocalisation compensates not only the energy of enolisation of the two carbonyl groups, but also the additional energy of rupture of the hydrogen bond, and this should naturally decrease the stability of the enol form and displace the equilibrium (relative to the 1,4-dihydroxy-derivatives) towards the diketone[78,86] (see Table 2). The representatives of this series which have been most studied

TABLE 2. Influence of the number of hydroxyl groups on tautomeric equilibrium in the naphthol series.

Formula of phenol	Keto-form	Conditions of tautomeric equilibrium	Composition of tautomeric mixture (% keto-form)	Refs.
	exists only as the phenol, but in a number of reactions exhibits the properties of the keto-form			78
		in the molten state; 200–210°	10.5	76
		in the molten state; 190–200°	17	78
		in the molten state; 200–210°	11	76
		1. in the molten state; 200–210° 2. boiling in acidic aqueous solution	67 19	76
		in the molten state; 200–210°	41	77
		exists almost entirely in the keto-form		76

are 1,2,5-trihydroxynaphthalene (α-hydrojuglone) and its 2-methyl homologue[76,77] †:



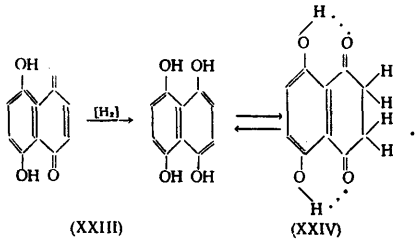
(XXI) (XXII)

The isomers (XXI) and (XXII) may exist in the equilibrium state in aqueous solution. The structures of both substances have been confirmed by spectroscopic data[76,87].

These regular features are shown even more clearly by 1,4,5,8-tetrahydroxynaphthalene, for which the conversion into the keto-form is accompanied by the production of two intramolecular hydrogen bonds. Accordingly, its keto--form (β-hydronaphthazarin) becomes more stable and this is naturally reflected in the properties of this compound.

† The diketone (XXII) — β-hydrojuglone — is present as glucosides in walnut extracts. Under the conditions of its extraction (boiling aqueous solution) it is partly converted into the enol--form — α-hydrojuglone[76].

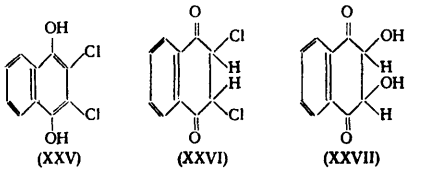
Thus 1,4,5,8-tetrahydroxynaphthalene (α-hydronaphthazarin) (XXIII), formed by the reduction of naphthazarin, is converted almost quantitatively under the conditions of the reaction into the isomeric β-hydronaphthazarin (XXIV):[88]



(XXIII) (XXIV)

The diketo-structure of β-hydronaphthazarin was proved by chemical methods[76,88]. Analogous behaviour is shown by the product of the reduction of quinizarin — leuco-quinizarin (1,2,3,4-tetrahydro-9,10-dihydroxy-1,4-diketoanthracene)[86,89]. The influence of the number of hydroxyl groups on tautomerism in the hydroxynaphthalene series is illustrated in Table 2.

A unique place in the 1,4-dihydroxynaphthalene series is occupied by compounds containing substituents (Hal, OH, SH, SO_3Na, etc.) capable of being removed. Here there are no reversible tautomeric transformations between the isomers, despite the fact that these compounds may exist in the individual state in both keto- and phenolic forms. These phenols are not converted into the diketones on fusion, since they usually decompose at elevated temperatures. On the other hand, the keto-forms, instead of enolising, are more readily converted into a quinonoid system with the removal of a molecule of an inorganic substance. Typical representatives of this type of compound are the isomeric 2,3-dichloro-1,4-dihydroxynaphthalene (XXV) and the dichlorodihydronaphthoquinone (XXVI). The latter readily loses a molecule of hydrogen chloride and is converted into 2-chloro-1,4-naphthoquinone[79].

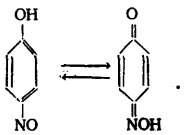


(XXV) (XXVI) (XXVII)

The keto-forms of these dihydroxynaphthalenes are in turn often obtained as a result of 1,2-addition to naphthoquinones[90-92]. Certain substituted diketones of the naphthalene series are nevertheless able to undergo irreversible enolisation — for example, (XVII) — but in these instances the reaction in this direction always competes with that involving elimination[93]. The individual properties of these compounds have been examined by Thomson[4].

3. TAUTOMERISM OF NITROSOPHENOLS

The introduction of electronegative substituents into the *ortho*- and *para*-positions of a phenol brings about a redistribution of the electron density in the molecule, leading to a decrease in the energy of aromatic conjugation and appreciable polarisation of the hydrogen–oxygen bond in the hydroxyl group. This facilitates the removal of hydrogen as a proton and leads to the appearance of keto–enol tautomerism. These features should be shown to the greatest extent in the nitrosophenol molecule, since the nitroso-group exhibits the greatest negative conjugation effect. Moreover, a distinguishing characteristic of the nitroso-group is its ability to combine with a proton using the unshared pair of electrons of the oxygen atom, with the formation of a hydroxyimino-group; this in turn should lead to additional stabilisation of the carbonyl form of the nitrosophenol as a result of the formation of a quinonoid system of conjugated bonds. Thus in the example which we are considering, there is on the one hand a decrease in the energy of aromatic conjugation in the phenolic form as a result of the presence of the nitroso-group and on the other hand an increase in the energy of enolisation of the carbonyl group, which is further stabilised by quinonoid conjugation. The final result of these two factors, operating in the same direction, is that in the nitrosophenol series the benzenoid (phenolic) form is less favoured than its isomeric quinone oxime form. Calculations by Jaffe[94] using the molecular orbital method showed that for 4-nitrosophenol the quinonoid state is favoured relative to the phenolic form to the extent of 4.6 kcal mole^{-1}. Experimental data published up to the present confirm that nitrosophenols exist chiefly in the quinonoid form. As a result, nitrosophenol $\rightleftharpoons$ quinone oxime tautomerism exhibits certain characteristic features compared with phenol–dienone tautomerism, particularly the marked sensitivity of the equilibrium to the medium, and the specific influence of substituents in the benzene ring:



Since in *o*-nitrosophenols an intramolecular hydrogen bond is formed, inevitably producing an additional influence on the characteristic features of the tautomeric equilibrium, we shall consider first the tautomerism of *p*-nitrosophenols.

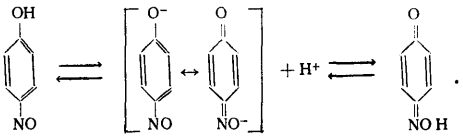
Facts indicating the tautomeric properties of *p*-nitrosophenol have been known for a long time. Bayer[95] as early as 1874, and later Goldsmidt[96], found that *p*-benzoquinone monoxime, formed by the reaction of *p*-benzoquinone with hydroxylamine, is identical in all respects to *p*-nitrosophenol obtained by the direct nitrosylation of phenol. It was found that in oxidation and reduction this compound behaves as a nitroso-compound, whereas on treatment with hydroxylamine it gives the quinone dioxime, that is, it reacts in the quinonoid form.

These data indicated the possibility of the reversible interconversion of *p*-nitrosophenol and *p*-benzoquinone monoxime. The first attempts to investigate the regular features of this transformation were undertaken using chemical methods[97-105] but no definite conclusions could be reached. The results obtained merely indicated the existence of a tautomeric equilibrium between the phenolic and

quinonoid forms. Thus it was shown that the phenolic form of nitrosophenols is converted into the quinonoid form by heating in the presence of acids [100,105] or by acidifying their alkaline solutions [106]. The two isomeric forms of the nitrosophenols give identical silver salts, which on treatment with methyl iodide give the methyl ethers of the benzoquinone oximes [102]. An analogous product is formed by the reaction of nitrosophenols with methyl sulphate in alkaline medium [102]. On the other hand, an attempt, using *p*-nitrophenylhydrazine, to determine the concentration of the quinonoid isomer in the products of the nitrosylation of phenol was unsuccessful, since all the nitrosophenol was converted into the corresponding *p*-nitrophenylhydrazone [102]. The reaction with diazomethane was found to be more suitable; diazomethane reacts with nitrosophenol in ether solution to give two products: glyoxime *NN'*-di-4-methoxyphenyl ether and benzoquinone 4-oxime *O*-methyl ether [104]. The results obtained could not be used, however, to determine the ratio of the tautomeric forms of the nitrosophenol. By 1930–1932 the opinion had been formed, on the basis of the above properties, that nitrosophenols exist chiefly in the phenolic form in the crystalline state and in inert solvents. Thus chemical methods proved unsuitable for the determination of the composition of tautomeric mixtures of nitrosophenols. The solution of these problems was made possible only by the application of spectroscopic methods, which without disturbing the equilibrium in the system, allowed its qualitative composition to be determined unambiguously and some information on its quantitative composition to be given.

The absorption spectrum of the products of the nitrosylation of phenols was first obtained by Hartley [107]. By comparing the spectrum of the products of the nitrosylation of phenol with the spectrum of *p*-nitrosoaniline, he established that the chief component of the mixture in ether solution is the quinonoid form. Baly [108], who repeated these studies, however, put forward the opposite opinion. This problem was later studied by Anderson [109]. By studying the absorption spectra of *p*-nitrosophenol in ether solution and comparing the results obtained with the spectra of the methyl ethers of the two isomeric forms of *p*-nitrosophenol, he showed that under these conditions the equilibrium mixture consists of approximately 70% quinone oxime and 30% nitrosophenol. Analogous results were obtained for solutions of nitrosophenol in dioxan, chloroform, and absolute alcohol. The most recent studies [110] of the infrared spectra of dilute solutions of *p*-nitrosophenol in carbon tetrachloride confirmed these data. When ultraviolet spectroscopy was applied to the study of the tautomerism of 2- and 3-substituted nitrosophenols, determination of the position of the maximum characteristic of the pure nitroso-form was found to be very difficult, since the equilibrium is generally displaced towards the quinonoid form and the more intense band due to the latter masks the band due to the nitroso--form. In this connection, the correctness of the interpretation of spectroscopic data in the determination of the characteristic features of the tautomerism of substituted nitrosophenols has been discussed [99,109,111,112].

The further development of spectroscopic methods has made it possible to return to this question and to solve the problem of determining the changes in the absorption spectra of the phenolic and quinonoid forms of nitrosophenols, irrespective of the number and nature of substituents [113]. In particular, detailed study of the spectroscopic properties of the products of the nitrosylation of phenol led a group of French workers [113–117] to recognise the existence of a three--component mixture in the tautomerism of nitrosophenols: the nitrosophenol, the quinone oxime, and an intermediate ionised form — the ambident ion‡:



Thus in the tautomerism of nitrosophenols, as in keto–enol tautomerism [1], the two forms first give up a proton with the formation of the same anion in each instance.

The use of spectroscopic methods has made it possible to establish the dependence of the equilibrium in a nitrosophenol–quinone oxime system on the nature of the solvent, the pH of the medium, and the position and nature of the substituents. In an aqueous medium, the above system of reversible transformations is considerably simplified and usually consists of two components. Moreover, under these conditions the tautomeric systems are extremely sensitive to changes in the pH of the medium only in the range from 3 to 7, and are independent of pH outside this range [112]. This phenomenon is associated with the ionisation of the two tautomers. In a strongly acidic medium (pH < 3), the ionisation should be suppressed, leading to a displacement of the equilibrium in one direction and the existence of only one neutral form, exhibiting the lowest acidity. In a strongly acidic medium this will in fact be the quinone oxime form. Similarly, in an alkaline medium (pH > 7) the un-ionised forms do not exist and in accordance with the total ionisation the intensity of the absorption becomes almost constant [112].

In a study of the ultraviolet spectra of aqueous solutions of unsubstituted *p*-nitrosophenol, the presence of two components (ionic and quinone oxime forms) in the system was confirmed by the existence of an isosbestic point [119]. These spectra were also used to calculate the dissociation constant of the oxime form ($pK = 6.21 \pm 0.03$); this quantity was also determined by conductimetric and potentiometric titration [119].

In neutral solvents, nitrosophenols exist in all three equilibrium forms, the quantity of ionic form increasing sharply with increase in the polarity of the solvent (ether, alcohol, water). The quantity of nitroso-form decreases and the proportion of oxime form increases in the same order [115].

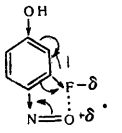
The introduction of alkyl substituents in the 2-position of the aromatic nucleus also increases the displacement of the entire system towards the quinonoid form. Thus in alcoholic solution, *p*-nitrosophenol and 3-methyl-4-nitrosophenol give maxima corresponding to all three forms (nitrosophenol, oxime, and ionic) with the oxime form predominating, whereas the introduction of alkyl substituents in the

‡ The *p*-nitrosophenol–quinone oxime tautomeric mixture was recently analysed by paper chromatography [118]. On the basis of the agreement between the calculated and experimental R_M values $\left(R_M = \log\left[\frac{1}{R_F} - 1\right]\right)$, it was assumed that the tautomeric mixture consists chiefly of nitrosophenol together with a small percentage of the oxime. No allowance was made, however, for the existence of the anionic form or for the exceptionally marked dependence of this equilibrium on the nature of the medium.

2-position leads to the disappearance or sharp decrease in the quantity of the nitroso-form in the equilibrium system [115]. Increase in the steric hindrance at the hydroxyl group, created by branched alkyl substituents, produces a completely quinonoid system — alcoholic solutions of these compounds contain only the oxime form [115]. This relationship has been studied in most detail by Finch [120] for 2,6-dialkylnitrosophenols where Alk = CH_3, C_2H_5, $CH(CH_3)_2$, or $C(CH_3)_3$. The opposite relationship is observed when the alkyl substituents are introduced into the 3,5-positions of the nitrosophenol. In this instance there is an increase in the proportion of the phenolic form in the tautomeric equilibrium in the order Alk = CH_3, C_2H_5, $CH(CH_3)_2$, and $C(CH_3)_3$. Branched substituents in the 3,5-positions apparently create additional steric hindrance to the conversion of the nitroso-form into the oxime form, and this naturally leads to an increase in the proportion of the benzenoid form [120].

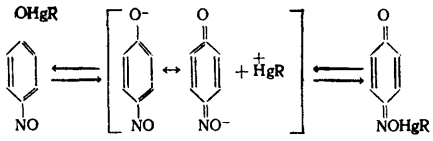
An analogous relationship is observed for the halogeno--derivatives of nitrosophenols. Thus the introduction of halogen into the 2-position of the aromatic nucleus displaces the equilibrium towards the oxime form [116]. An alcoholic solution of 2,6-dichlorobenzoquinone oxime con tains only the oxime form with a small quantity of the ionised form. The same is observed for the corresponding bromo-derivatives [117]. The introduction of halogen into the 3-position, however, leads to a decrease in the proportion of the quinone oxime form in the equilibrium [115]

A unique position among halogeno-derivatives of *p*-nitrosophenols is occupied by 3-fluoro-4-nitrosophenol. This phenol cannot be converted into the isomeric 3-fluorobenzoquinone oxime. When its alkaline solution is heated and then acidified, the nitroso-form is precipitated unchanged [106]. This phenol also exists only in the nitroso--form in acidic and neutral media, irrespective of the nature of the solvent [121]. Spectroscopic studies [106] of 3-fluoro-4-nitrosophenol indicate extensive polarisation of the nitroso-group, leading to the formation of a partly bipolar structure, which by interaction of the fields may form a characteristic five-membered ring. With this bipolar structure, the oxygen atom of the nitroso-group is apparently unable to combine with a proton from the medium:



The regular features of the tautomeric equilibrium are not altered significantly on going from *p*-nitrosophenol to 4-nitrosonaphth-1-ol. With this also, the oxime form predominates in polar solvents [122], the ionic form predominates in alkaline medium [123], and the oxime form predominates in the solid state [124].

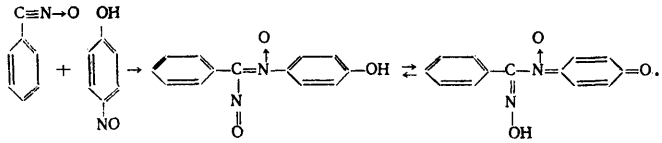
Tautomerism is also shown by the alkylmercury derivatives of *p*-nitrosophenols. In a study of the infrared spectra of these compounds, Nesmeyanov and Kravtsov [125] found that the intensity of the band due to the nitroso-group shows a definite relationship to the nature of the solvent and is independent of the concentration of substance. Since the infrared spectra indicate that in the solid state the alkylmercury derivatives of nitrosophenols have the quinone oxime structure, the observed phenomenon must be due to the existence of a tautomeric equilibrium with the intermediate formation of a common anion:



This feature is also shown by nitrosophenols with substituents in the ring, the introduction of alkyl substituents in the 2-position leading to a decrease in the concentration of the nitroso-form of the alkylmercury derivative in the solution.

An interesting feature is that interconversion of the isomers is also possible for the *O*-acetyl derivatives of nitrosophenols. For example, *O*-acetylnitrosophenol is converted quantitatively into the more stable *O*-acetylbenzoquinone oxime on recrystallisation [116].

Among other nitrosophenol derivatives, the possibility of tautomerism is observed in the products of the condensation of nitrosophenols with the oximes of certain nitriles; the 4-nitrosophenol derivative exists chiefly in the phenolic form, whereas the 1-nitrosonaphth-2-ol derivative exists in the quinonoid form [126]:

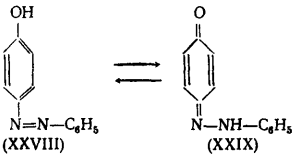


The regular features of the tautomerism of nitrosophenols are slightly different for the *ortho*-isomers. This is due to the existence [127] in these substances of an intramolecular hydrogen bond which has a fairly strong stabilising action on the nitroso-group, so that the energetic relationships between the phenolic and quinonoid (here, *ortho*--quinonoid) structures is altered slightly and the benzenoid form of the nitrosophenol is preferred. The ultraviolet spectra [127] show that *o*-nitrosophenol exists only in the phenolic form in non-polar solvents. The introduction of substituents exhibiting positive conjugation effects into the *para*-position relative to the nitroso-group, however, facilitates the rearrangement of the nitroso-group into the oxime group. Thus 2-nitroso-5-methoxyphenol and 2-nitroso--5-dimethylaminophenol [127] exist in solution in the form of tautomeric mixtures; the quinonoid form predominates, and its concentration increases with increase in the polarity of the solvent. These spectroscopic data agree with certain chemical properties. In particular, the crystallisation of 2-nitroso-5-methoxyphenol [128] from ethanol and benzene gives crystals with different appearance and melting points. These were assumed to be two tautomeric forms. With the *o*-nitrosophenols of the naphthalene series (1-nitrosonaphth-2-ol and 2-nitrosonaphth-1-ol) there is tautomeric equilibrium with the nitroso-form predominating [129].

4. TAUTOMERISM OF AZOPHENOLS

The azo-coupling of phenols, together with the data obtained by Zincke [130], who showed that hydroxyazo-compounds with analogous structure are formed by the action of arylhydrazines on the corresponding quinones, indicated the

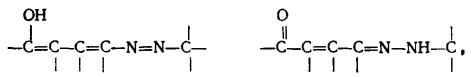
possibility of tautomeric equilibrium between azophenols and quinone arylhydrazones. A number of authors [131-138] suggested that this equilibrium is an ordinary prototropic transformation with migration of a proton between the nitrogen atom and the phenolic oxygen. This transformation is accompanied by rearrangement of the benzenoid bond system into a quinonoid system or by the opposite rearrangement of the quinonoid system into the benzenoid system:



(XXVIII) (XXIX)

The first studies of this tautomerism by chemical methods were carried out in 1929, when Borshe and coworkers [139] used dinitrophenylhydrazine to isolate the hydrazone form (XXIX) as the dihydrazone from the tautomeric mixture. The results obtained were not conclusive, since the dihydrazone can be formed directly from the monohydrazone by heating in acidic medium. Attempts to prove the existence of tautomerism in the azophenol series by chemical methods include the use of the reaction with cyclopentadiene, which according to the diene synthesis scheme gives the products of the addition to the quinonoid ring of the hydrazone form [140]. Direct confirmation of tautomerism in the azophenol series by isolation of both tautomeric forms from the equilibrium mixture has not been obtained. Only the use of spectroscopic methods made it possible to study effectively the regular features of the tautomerism of azophenols [141-152]. The successful solution of this problem was greatly assisted by the distinct separation of the spectroscopic characteristics of these tautomeric forms in the ultraviolet range.

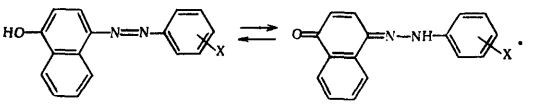
The energetic relationships for the formation of the two forms (azophenol and quinone hydrazone) facilitate tautomerism to a greater extent than in the unsubstituted phenols. Summation of the bond energies of the systems



gives 432 kcal mole^{-1} for the enol-form and 456 kcal mole^{-1} for the keto-form, that is, the formation of the keto-form is favoured to the extent of 24 kcal mole^{-1}. Thus the energy of enolisation of the carbonyl form (particularly with allowance for the quinonoid conjugation) of the azophenols is much greater than the energy of enolisation required in the formation of unsubstituted phenols, leading to a lower stability of the aromatic system. Hence the factors determining the appearance of tautomerism in the phenol series (see p. 818) should be shown even more clearly in the azophenols. The accumulation of aromatic rings condensed with the azophenol nucleus does in fact lead to more rapid conversion of the phenols into the isomeric quinonoid compounds. Thus in the solid state, compounds of the benzene series exist in the benzenoid form, whereas derivatives of the naphthalene and anthracene series exist only in the quinonoid form [149]. In solutions this change is more regular [150,153]. For example, 4-phenylazophenol always exists in only one form and exhibits a single absorption maximum (343 nm) corresponding to the azo-form, whereas 4-phenylazonaphth-1-ol and 4-phenylazoanthr-1-ol show maxima corresponding to the azophenol form (392 and 442 nm respectively) and the quinone hydrazone form (475 and 506 nm). Finally, 9-phenylazoanthr--10-ol shows only one maximum in the ultraviolet range, corresponding to the quinone hydrazone form [151]. Thus among the *p*-azophenols which we have considered, tautomeric equilibrium is found only in the derivatives of 4-azonaphthols and related compounds.

The influence of the nature of the substituents on the tautomerism of azophenols is also shown extremely clearly. Here, all the regular features characteristic of the tautomerism of phenolic compounds are preserved. The introduction of electron-accepting substituents into the molecule leads to an increase in the concentration of the keto-form, whereas the presence of electron-donating substituents facilitates the production of aromatic properties in the ring and displaces the equilibrium towards the phenolic structure. It should be noted that tautomerism is found only in the phenyl(or aryl)azophenols, but not in alkylazophenols. This is due to the fact that the phenylazo-group produces a greater displacement of electrons into the aromatic ring of the phenol, facilitating the removal of a proton and conversion into the carbonyl form. A similar influence is shown by the introduction of substituents into the phenyl nucleus of the hydrazone.

All the regular features of the influence of substituents on the tautomeric equilibrium have been studied for 4-azonaphth-1-ol derivatives:



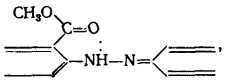
The data [154-156] in Table 3 show the influence of substituents in the phenyl ring of the hydrazone on the tautomeric azophenol $\rightleftharpoons$ quinone hydrazone system. The ratio of the extinctions ($\epsilon_{hydrazo}/\epsilon_{azo}$) indicates approximately the proportions of the tautomers in the equilibrium mixture. Electron-donating substituents decrease this ratio, that is, they decrease the proportion of hydrazo-form, whereas electron--accepting substituents increase this ratio. A characteristic feature is that the introduction of substituents in the 2-position usually increases the proportion of the hydrazone tautomer to a much greater extent than the introduction of an analogous group in the 4-position. This anomaly is related to the possibility of intramolecular hydrogen bond formation. Thus the introduction of a carboxyl group in the 2-position [157] stabilises the hydrazone form as a result of the formation of an intramolecular hydrogen bond. Maximal stability of the keto-form, as expected, is shown by the 2,4-dinitrophenylhydrazones. Here the negative conjugation effect of the substituent in the phenol molecule

TABLE 3. Influence of substituents on the tautomerism of azonaphthols.

Substituent X	4-Arylazonaphth-1-ol $\epsilon_{hydrazo}/\epsilon_{azo}$	1-Arylazonaphth-2-ol $\epsilon_{hydrazo}/\epsilon_{azo}$	Substituent X	4-Arylazonaphth-1-ol $\epsilon_{hydrazo}/\epsilon_{azo}$	1-Arylazonaphth-2-ol $\epsilon_{hydrazo}/\epsilon_{azo}$
4′-NH_2	—	0.17	3′-OCH_3	0.89	1.41
4′-OH	—	0.40	3′-Cl	1.50	—
4′-OCH_3	0.22	0.45	3′-NO_2	1.90	2.0
4′-CH_3	0.39	1.08	2′-CH_3	0.23	1.71
H	0.63	1.31	2′-Cl	0.50	—
4′-Cl	0.84	1.26	2′-OCH_3	0.90	2.0
4′-NO_2	2.0	2.00	2′-NO_2	2.0	2.0
4′-$COOCH_3$	2.0	—	2′-$COOCH_3$	2.0	—

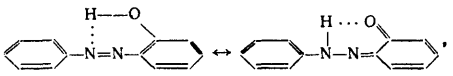
increases to such an extent that tautomerism is possible in mononuclear azophenols [140].

In the 4-phenylazonaphth-1-ol series, the NH and OH groups present in the hydrazo- and azo-tautomeric forms, are able to form hydrogen bonds with the solvent. Since these bonds have different strengths, the tautomers may be stabilised by these bonds to different extents. Moreover, substituents in the 2-position of the benzene ring will also influence the strength of the hydrogen bonding with the solvent, either by the formation of intramolecular hydrogen bonds of the type



or by creating steric hindrance to the formation of an intermolecular hydrogen bond. The influence of solvents on the tautomeric equilibrium has also been studied [148] for 4-phenylazonaphth-1-ols. For the 3'- and 4'-substituted compounds the concentration of the hydrazone tautomer increases with increase in the polarity of the solvent in the order: hexane < benzene < chloroform < 50% ethanol < < CH_3COOH. The picture is complicated considerably in the presence of 2-substituents capable of forming intramolecular hydrogen bonds (Cl, OCH_3, etc.). The proportion of hydrazo-form is smaller in polar solvents (water, ethanol, CH_3COOH) than in hexane, benzene, and chloroform. An explanation for this anomaly is apparently to be found in the competition between intramolecular and intermolecular hydrogen bond formation.

In the tautomerism of *o*-azophenols, the energetic relationships favour the formation of the carbonyl form to an even greater extent, again as a result of the production of an intramolecular hydrogen bond. As a result of this additional factor, tautomeric equilibrium is established between two isomeric forms even in solutions of 2-phenylazophenol [150]. It should be recognised that in *o*-phenylazophenol and *o*-phenylazonaphthols, intramolecular hydrogen bonding should also be shown by the phenolic form. It was first assumed [136,137,158,159] that these substances do not exhibit tautomeric properties, for the presence of the intramolecular hydrogen bond leads to the production of a mesomeric hybrid of the type:



that is, a delocalised hydrogen bond should be formed. Later spectroscopic studies [148,155,160] showed, however, that the system contains both isomers and that the intramolecular hydrogen bond is essentially static, leading to polarisation of the molecule and facilitating tautomerism.

The action of the other factors influencing the tautomeric equilibrium of *o*-azophenols is the same as that for *p*-azophenols. Table 3 gives data characterising the influence of the nature and position of substituents for 1-phenylazonaphth-2-ol. The effect differs little from those observed in the *para*-derivatives. The introduction of electron-donating substituents again displaces the equilibrium towards the azo-form and the introduction of electron-accepting substituents displaces it towards the hydrazo-form [155,156].

Table 4 gives data showing the influence of solvent on the equilibrium system for 1-(4-methoxy-3,5-dimethylphenylazo)naphth-2-ol and compares the results with those

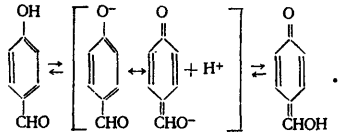
TABLE 4. Influence of solvent on the equilibrium for 1-(4-methoxy-3,5-dimethylphenylazo)-naphth-2-ol.

Solvent	Azo-compound $\varepsilon_{azo}/\varepsilon_{hydrazo}$	$CH_3COCH_2COOC_2H_5$ C_{enol}/C_{ketone}	$CH_3COCH_2COCH_3$ C_{enol}/C_{ketone}
Water	—	0.004	0.24
50% acetic acid	0.445	—	—
50% ethanol	0.556	—	—
CH_3COOH	0.570	0.061	2.8
75% ethanol	0.684	—	—
$CHCl_3$	0.764	0.089	3.8
87.5% ethanol	0.795	—	—
$C_6H_5NO_2$	1.040	—	—
C_6H_5OH	1.130	0.150	5.3
Pyridine	1.150	0.220	—
Benzene	1.160	0.220	5.7
CCl_4	1.350	—	—
n-Hexane	2.120	0.900	12.0

for the equilibrium constants (C_{enol}/C_{ketone}) for acetoacetic ester and acetylacetone [155]. There is a complete analogy in the influence of the substituents (Table 4). In all series the keto-structures are present in higher concentration in the more polar solvents.

5. EQUILIBRIUM PHENOL–QUINONOID TRANSFORMATIONS OF *p*-SUBSTITUTED PHENOLS

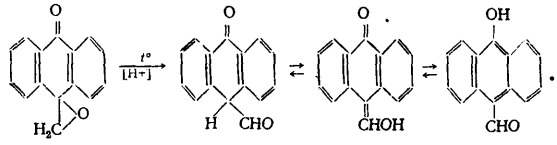
As already noted, the presence of electron-accepting groups in a phenol molecule should facilitate phenol–quinonoid tautomerism. In principle, this property may be shown by any phenol containing carbonyl, carboxyl, carbalkoxyl, nitrile, nitro- and other analogous groups in the *para*-position and, to a lesser extent, in the *ortho*-position. For example, for *p*-hydroxybenzaldehyde this transformation might be represented by the following equilibrium:



The displacement of the electrons in the aromatic ring under the influence of the negative conjugation effects of these substituents is generally insufficient, however, for the formation of a compound with a quinonoid bond system. Usually, this transformation requires the additional influence of other factors on the phenol molecule. The greatest influence in this direction is shown by steric hindrance, the decrease in the aromaticity of the phenol nucleus in condensed systems, and binding of the phenolic hydrogen by the medium. In the last, reversible equilibrium between the neutral phenolic form and a quinonoid anion may be established.

Published data show that the existence of the above tautomeric systems is possible. Thus study of the rearrangement of the epoxide of 9-methylene-10-anthrone [161,162] gave a yellow-orange substance with m.p. 206–208°, which according to the method of preparation and analysis should be 9-formyl-10-anthrone. The high acidity of the product (its strength is close to that of benzoic acid) indicates, however,

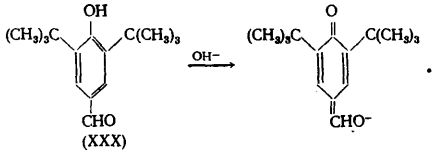
that it is present in equilibrium with the hydroxy-forms 9-formyl-10-anthrol and 9-hydroxymethylene-10-anthrone.



The existence of this ternary equilibrium was also confirmed by chemical and spectroscopic methods [162].

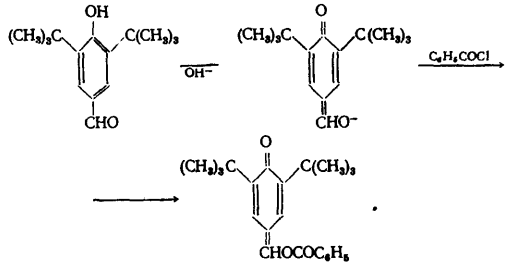
On going to the benzene series, it is difficult to reach definite conclusions regarding the tautomerism of hydroxybenzaldehyde. Thus Bartel [163], in a polarographic study of *p*-hydroxybenzaldehyde at pH 5.4–7.2 detected two polarographic waves similar to dissociation waves. These could not be attributed to ionised and un-ionised forms of the aldehyde, however, since the dissociation of *p*-hydroxybenzaldehyde in this pH range is too small. Even in a strongly alkaline medium, only neutral molecules are depolarised at the cathode. The existence of two waves might be attributed to tautomerism, but the absence of direct experimental data makes this suggestion extremely hypothetical.

The greatest quantity of material has appeared in connection with the study of the properties of phenols exhibiting steric hindrance. This is not surprising, in view of the general tendency for 2,6-disubstituted phenols and their derivatives to form stable quinonoid or quinolide structures [164–166]. The most typical compound in this respect is 3,5-di-t-butyl-4-hydroxybenzaldehyde (XXX), which exhibits extremely specific properties in an alkaline medium. Thus unlike the unsubstituted 2,6-di-t-butylphenol, it dissolves readily in alkalis, and this can be attributed only to the formation of a phenoxide ion in the isomeric dienone–enolate form. Careful neutralisation of alkaline solutions of this aldehyde leads to the quantitative separation of the aldehyde form [167]:



Spectroscopic studies [167,168] of alkaline solutions of (XXX) also indicate formation of the enolate form. When the aldehyde (XXX) is dissolved in alkalis, the absorption maximum in the ultraviolet spectrum (λ_{max} = 290 nm) is displaced towards longer wavelengths (λ_{max} = 370 nm). Absorption in this range is characteristic [169] of certain quinone methides and alkoxy-derivatives of quinone methides, with analogous structure. The infrared spectrum of an alkaline solution of (XXX) does not contain the band corresponding to an aromatic aldehyde, but shows an absorption band characteristic of conjugated carbonyl in quinone methide compounds, usually observed as an averaged band at 1618 cm^{-1} or split to form a doublet [170,171] in the region of 1610–1630 cm^{-1}. Finally, isolation of the sodium salt of 3,5-di-t-butyl-4-hydroxybenzaldehyde in crystalline form [167] showed that this compound also gives only the quinonoid bond system.

The quinonoid structure of the salt of the benzaldehyde (XXX) is also confirmed by chemical reactions. When the finely ground salt is heated in dry hexane with benzoyl chloride in a current of inert gas, the only product is 2,6-di-t-butylbenzoylhydroxyquinone methide [167]. The reaction with an alkaline solution of the benzaldehyde is analogous [168]:



These properties of 3,5-di-t-butyl-4-hydroxybenzaldehyde cannot be related to typical tautomerism, since in this example, as for phloroglucinol (see p. 820), the equilibrium apparently involves the un-ionised phenolic form and the dienone–enolate anion, whose formation is due to the transfer of the negative charge to the *p*-substituent from the strongly polarised π-electron bond.

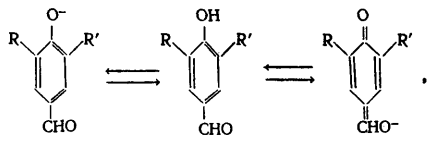
Properties analogous to those of 3,5-di-t-butyl-4-hydroxybenzaldehyde are shown by certain other 3,5-dialkyl-4-hydroxybenzaldehydes. Nikiforov and Ershov [167] recently studied the influence of alkyl substituents on the equilibrium between these aldehydes and their salts. The infrared spectra of solid specimens showed that the salts of 3,5-di-t-butyl-4-hydroxybenzaldehyde (XXX; R = R′ = CMe_3), 4-hydroxy-3,5-di-isopropylbenzaldehyde (XXXI; R = R′ = $CHMe_2$), and 5-t-butyl-4-hydroxy-3-methylbenzaldehyde (XXXII; R = CH_3, R′ = CMe_3) have a quinonoid structure, whereas salts of *p*-hydroxybenzaldehyde (XXXIV; R = R′ = H) and 4-hydroxy-3,5-dimethylbenzaldehyde (XXXIII; R = R′ = CH_3) exist in the phenoxide form. Salts of the aldehydes (XXX), (XXXI), and (XXXII) in solution naturally may not have the classical quinonoid structure, since the distribution of the negative charge should be influenced significantly by the solvation of the entire molecule as a whole. There is no doubt, however, that the structure of these anions is close to the quinonoid structure, and this is responsible in particular for the ready solubility of these aldehydes in aqueous alkalis. This conclusion is confirmed by the ultraviolet spectra of the alkaline solutions and also by the equilibrium constants for the formation of the salts of 3,5-dialkyl-4-hydroxybenzaldehydes (Table 5).

For 3,5-dialkyl-4-hydroxybenzaldehydes exhibiting steric hindrance, the value of the constant is smaller and decreases monotonically with decrease in the steric hindrance at the phenolic hydroxyl, but it subsequently increases sharply on

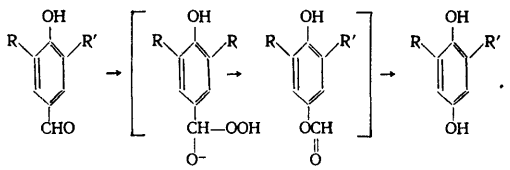
TABLE 5. Ultraviolet spectra and ionisation constants of 4-hydroxybenzaldehydes.

Compound No.	4-Hydroxy-3,5-dialkylbenzaldehyde	Ultraviolet spectra λ_{max} neutral	Ultraviolet spectra λ_{max} alkaline	Δλ	$10^9 K$
XXX	3,5-di-t-butyl	290	367	77	4.21
XXXI	3,5-di-isopropyl	290	356	66	3.80
XXXII	3-methyl-5-t-butyl	290	358	68	2.51
XXXIII	3,5-dimethyl	289	351	62	8.51
XXXIV	4-hydroxybenzaldehyde	285	336	51	11.48

going to the aldehyde with methyl substituents and the unsubstituted *p*-hydroxybenzaldehyde, and increases further



in the reverse order. For phenols as a whole, a decrease in dissociation constant with increase in the steric hindrance at the phenolic hydroxyl is characteristic. An analogous phenomenon is also observed in the formation of phenoxide salts of the hydroxyaldehydes (XXXIII) and (XXXIV), but the observed reverse relationship in compounds (XXX)–(XXXII) is due to the fact that the steric factor facilitates the phenol–dienone bond rearrangement and hence facilitates the formation of the quinonoid anion. These conclusions agree with data obtained from the infrared spectra of salts of *p*-hydroxybenzaldehydes and are confirmed by certain chemical reactions of these compounds, taking place in alkaline medium [172]. The most characteristic in this respect is Dakin's reaction. According to the mechanism accepted at present [173,174], this reaction passes through a stage involving the addition of hydrogen peroxide to the carbonyl group:



In practice, a marked decrease in the reaction rate is observed for hydroxyaldehydes with bulky alkyl substituents [172]. This is apparently due to the fact that these hydroxyaldehydes in alkaline medium (the conditions of Dakin's reaction) exist chiefly in the quinonoid–enolate form.

The influence of steric hindrance at the phenolic hydroxyl on the ease of formation of the quinonoid bond system has been followed most thoroughly in a study of the equilibrium between hydroxyphenyldiazonium salts and quinonediazides [174,175]:

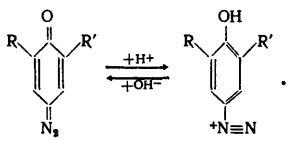


TABLE 6. Influence of substituents on the equilibrium conversion of quinone diazides into diazonium salts.

2,6-Dialkyl-*p*-quinone diazide	p*K*
p-Quinone diazide	3.19
2,6-Dimethyl	2.83
2-Methyl-6-t-butyl	2.72
2,6-Di-isopropyl	2.76
2,6-Di-t-butyl	1.65

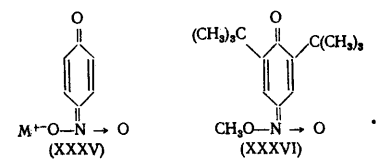
TABLE 7. Influence of *para*-substituents on the displacement of the absorption maximum in the ultraviolet spectrum of 4-substituted 2,6-di-t-butylphenols.

R	2,6-Di-t-butyl-4-R-phenol			R	2,6-Di-t-butyl-4-R-phenol		
	neutral, λ_{max}	alkaline, λ_{max}	$\Delta\lambda$		neutral, λ_{max}	alkaline, λ_{max}	$\Delta\lambda$
$C(CH_3)_3$	223	251	28	$COOC_2H_5$	261	324	63
CH_3	222	250	28	$COCH_3$	284	363	79
H	214	244	30	CN	252	307	55
Br	226	257	31	CHO	293	370	77
$CONH_2$	258	321	63	NO_2	325	450	125

The data [175] in Table 6 show that with increase in the steric hindrance at the phenolic hydroxyl, the equilibrium is displaced towards the formation of the quinonoid bond system, so that conversion of the quinonediazide into the diazonium salt requires an increasingly acidic medium. A characteristic feature is that the stability of the quinonediazides in the solid state increases in the same order [176].

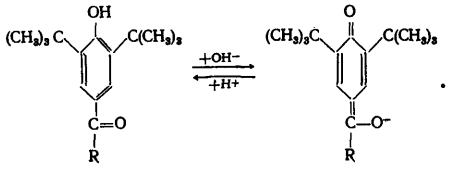
Since *o*-t-alkyl groups favour the formation of the quinonoid system to the greatest extent, a spectrophotometric study was made of the influence of various substituents on the behaviour of 4-substituted 2,6-di-t-butylphenols in alkaline medium [177,178]. The magnitude of the bathochromic shift (Table 7), which provides a criterion of the formation of a quinonoid system, increases with increase in the negative conjugation effect of the substituent, and differs considerably from the shift produced on the formation of ordinary phenoxide ions. In these examples we must naturally have in mind only the preferential location of the negative charge on the *para*-substituent. For phenols which do not contain alkyl substituents in the *ortho*-positions, the corresponding values of $\Delta\lambda$ are smaller, indicating greater delocalisation of the electron density throughout the molecule as a whole.

The greatest difference in absorption in alkaline medium is shown by 2,6-di-t-butyl-4-nitrophenol. The possibility of the reverse conversion of the neutral phenolic form of nitrophenols into the ionised quinonoid *aci*-form is also confirmed by certain chemical data. Thus *p*-nitrophenol salts which have been isolated are assigned the structure (XXXV): [179-181]

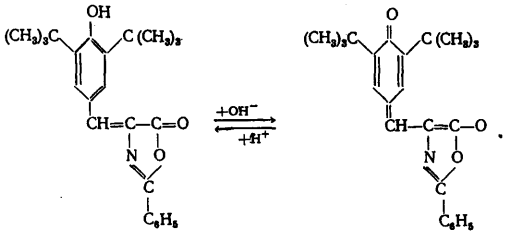


Methylation of 2,6-di-t-butyl-4-nitrophenol [177] gave a compound to which, on the basis of its chemical properties and spectroscopic data, was assigned the ether structure (XXXVI). It should be noted that in the methylation of 2,6-di-t-butyl-4-cyanophenol, only the normal *O*-methyl ether was isolated. The difference evidently excludes the influence of steric hindrance on the direction of the methylation of this nitrophenol. Finally, early papers [182] describe the methyl ether of the quinonoid form of *o*-nitrophenol. Unfortunately, the problems of reversible transformations in the nitrophenol series have as yet been insufficiently studied, so that no conclusions can be reached regarding the tautomeric transformation of nitrophenols.

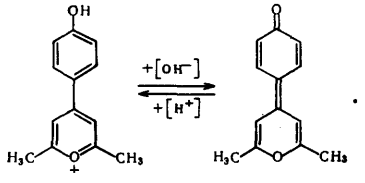
Spectroscopic data and the anomalous solubility in alkalis indicate [170,178,183] the existence of an equilibrium in the formation of salts of 4-benzoyl-, 4-cyano-, and 4-carbethoxy--2,6-di-t-butylphenols.



An analogous phenomenon is apparently observed in the formation of salts of 4-(3,5-di-t-butyl-4-hydroxybenzylidene)-2-phenyl-5-oxazolone [184]:

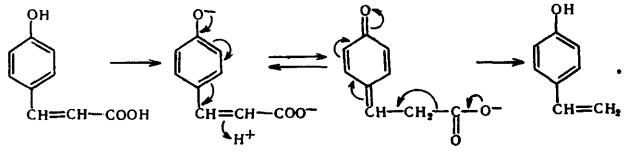


Very interesting behaviour in alkaline medium is shown by certain pyrylium salts containing phenolic substituents in the 4-position. Here the formation of the phenoxide ion should give a compound with a bipolar structure, with opposite charges on the oxygen atoms, established by the quinonoid conjugation extending over both rings [185].

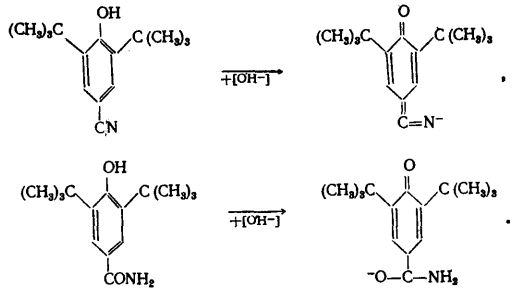


4-Substituted phenols on the whole show a distinct tendency to form a quinonoid bond system in reactions involving these substituents. These transformations are generally not tautomeric, however, but are related to the equilibrium between the ionised and un-ionised substance. Such transformations apparently explain the influence of the steric factor, facilitating formation of the quinonoid system, on the decarboxylation of *p*-hydroxycinnamic acids [186], the hydrolysis of *p*-hydroxybenzamides and nitriles [187], and the hydrolysis of the corresponding *N*-benzoyltyrosines and *N*-benzoyltyramines [188], taking place in alkaline medium.

In weakly alkaline solution, *p*-hydroxycinnamic acid is decarboxylated fairly rapidly, the reaction rate decreasing at pH < 9. This phenomenon can be attributed to the fact that protonation of the doubly-charged anion produces a quinonoid structure, which undergoes rapid decarboxylation:



The maximum corresponding to aromatic absorption in the ultraviolet spectrum of *p*-hydroxycinnamic acid in alkaline medium is displaced by 35 nm (310 nm → 345 nm), and this may indicate the presence of the quinonoid anion. This displacement is twice as large for 3,5-di-t-butyl-4-hydroxycinnamic acid (70 nm); the alkaline solution acquires a yellow colour, which disappears on acidification. The doubly-charged anion of this acid evidently exists in the quinonoid form. Its decarboxylation at pH 8.5 is 2.5 times faster than that of unsubstituted *p*-hydroxycinnamic acid [186]. An approximately analogous influence of the steric factor is observed in the hydrolysis of the amides and nitriles of the corresponding benzoic acids. Table 8 gives the rates of hydrolysis [187] of the benzamides and benzonitriles in alkaline medium. Comparison of the rates shows that the hydrolysis of 4-hydroxybenzamides and nitriles is 30 times faster than hydrolysis of their 4-hydroxy-3,5-di-t-butyl analogues. The rate of hydrolysis increases sharply for the 4-methoxy-derivatives. These facts are in good agreement with the assumption that an anion with the quinonoid structure exists under the conditions of the reaction:



The hydrolysis of *N*-benzoyltyrosines and *N*-benzoyltyramines is more complex [188]. These compounds are of interest since it is possible to establish a dienone structure with the formation of spirocyclic systems. Here again, the influence of the steric effect is clearly shown. Thus the rate of hydrolysis of 3,5-di-t-butyl-*N*-benzoyltyrosine is about half the rate of hydrolysis of *N*-benzoyltyrosine, and the corresponding rates for substituted and unsubstituted benzoyltyramines differ by a factor of 7.

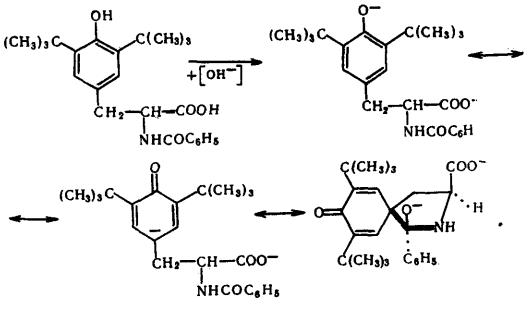
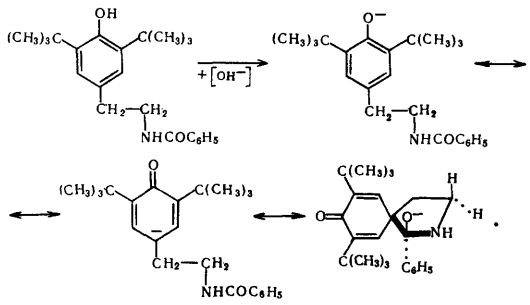


TABLE 8. Rate constants for the hydrolysis of benzamides and benzonitriles.

Compound		$10^6 K$, min^{-1}
Benzamides	4-hydroxy	63
	4-methoxy	963
	4-hydroxy-3,5-di-t-butyl	2
	4-methoxy-3,5-di-t-butyl	505
Benzonitriles	4-hydroxy	125
	4-methoxy	3000
	4-hydroxy-3,5-di-t-butyl	4
	4-methoxy-3,5-di-t-butyl	2000

The formation of a labile spirodienone should decrease the concentration of the *N*-benzoyl derivative, suitable for attack by an external base. The ratio of the rates shows that this factor increases in the tyramine series, since the formation of the spirodienone is then favoured to a greater extent in the hydrolysis of *N*-benzoyltyrosines:



---o0o---

Tautomeric transformations in the phenol series are extremely interesting, since the phenomenon of tautomerism, which is widely encountered in organic chemistry, is here associated with the breakdown of an aromatic bond system. On the other hand, the questions examined above may also be useful for an understanding of many of the transformations of phenols and their derivatives, of definite practical importance. Unfortunately, most work on the tautomerism of phenolic compounds is chiefly qualitative in character. The investigation of strict quantitative relationships governing this phenomenon will undoubtedly be of considerable interest.

1. M.I.Kabachnik, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 7, 263 (1962).
2. V.V.Ershov, A.A.Volod'kin, and G.N.Bogdanov, Uspekhi Khim., 32, 154 (1963) [Russ.Chem.Rev., 75 (1963)].
3. T.I.Temnikova, "Kurs Teoreticheskikh Osnov Organicheskoi Khimii" (Theoretical Principles of Organic Chemistry), Goskhimizdat, Leningrad, 1962, p.572.
4. R.Thomson, Quart.Rev., 10, 27 (1956).
5. G.A.Zlobina and V.V.Ershov, Izv.Akad.Nauk SSSR, Ser. Khim., 1666 (1964).
6. C.D.Nenitzescu, "Organic Chemistry" (Translated into Russian), Inostr.Lit., Moscow, 1962, Vol.1, p.478.
7. V.V.Ershov and A.A.Volod'kin, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 730 (1962).
8. A.A.Volod'kin and V.V.Ershov, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 2022 (1962).
9. M.Kharasch and B.Joshi, J.Org.Chem., 22, 1439 (1957).
10. Cited by H.Zollinger in "Advances in Physical Organic Chemistry" (Edited by V.Gold), Academic Press, New York, Vol.2, p.182.
11. J.Conant and G.Kistiakowsky, Chem.Rev., 20, 191 (1937).
12. E.Müller, "Neuere Anschauungen der organischen Chemie" (Translated into Russian), Inostr.Lit., Moscow, 1960, p.428.
13. J.Franklin, J.Amer.Chem.Soc., 72, 4278 (1950).
14. J.Conant and A.Thompson, J.Amer.Chem.Soc., 54, 4039 (1932).
15. V.Prelog, J.Chem.Soc., 420 (1950).
16. V.Prelog, K.Wiesner, W.Ingold, and O.Haffigen, Helv. Chim.Acta, 31, 1325 (1948).
17. F.Fawcett, Chem.Rev., 47, 219 (1950).
18. K.Mayer, Annalen, 379, 37 (1911).
19. E.Talelem and S.Pappas, J.Amer.Chem.Soc., 85, 173 (1963).
20. A.Burgstahler, O.Abdel-Rahman, and Pina-Lu Chien, Tetrahedron Letters, 61 (1964).
21. T.Coffild, U.S.P. 2903487 (1959); Ref.Zhur.Khim., 3L85 (1961).
22. T.Coffild, U.S.P. 2903346 (1959); Ref.Zhur.Khim., 24L167 (1961).
23. N.Kornblum and A.Lurie, J.Amer.Chem.Soc., 81, 2705 (1959).
24. N.Kornblum and R.Seltzer, J.Amer.Chem.Soc., 83, 3668 (1961).
25. T.Coffild, A.Fielbey, E.Ecke, and A.Kolka, J.Amer.Chem. Soc., 79, 5019 (1957).
26. G.Wheland, J.Chem.Phys., 1, 731 (1933).
27. E.Vischer, J.Chem.Soc., 815 (1953).
28. L.Asp and B.Lindberg, Acta Chem.Scand., 4, 1192 (1950).
29. B.Lindberg, Acta Chem.Scand., 5, 885 (1951).
30. H.Erdtman, Proc.Roy.Soc., 143A, 191 (1933).
31. G.Merling, Annalen, 278, 20 (1894).
32. F.Bean and T.Donovan, U.S.P. 2376112 (1945); Chem. Abs., 39, 4630 (1945).
33. J.Pollak, Monatsh., 14, 419 (1893).
34. H.Hlasiwetz, Annalen, 119, 202 (1861).
35. B.Tschoubar, "The Mechanisms of Organic Reactions" (Translated into Russian), Inostr.Lit., Moscow, 1963, p.186.
36. A.Bayer, Ber., 19, 159 (1886).
37. V.Farmer and R.Thomson, Chem.and Ind., 86 (1956).
38. N.Kananiva, Ann.Report Fac.Pharm., Kanazawa Univ., 4, 10 (1954); Chem.Abs., 50, 11273 (1956).
39. N.Kananiva, J.Pharm.Soc.Japan, 75, 670 (1955).
40. J.Herzig and B.Erthal, Monatsh., 31, 827 (1910).
41. A.Spitzer, Monatsh., 11, 104 (1890).
42. A.Spitzer, Monatsh., 11, 287 (1890).
43. K.Margulies, Monatsh., 9, 1046 (1888).
44. K.Margulies, Monatsh., 10, 459 (1889).
45. J.Herzig, F.Wenzel, and K.Harnstein, Monatsh., 27, 786 (1906).
46. J.Herzig and S.Zeisel, Monatsh., 9, 221 (1888).
47. J.Herzig and S.Zeisel, Monatsh., 9, 893 (1888).
48. J.Herzig and B.Erthal, Monatsh., 32, 470 (1911).
49. A.Jain and T.Seshadi, Proc.Indian Acad.Sci., 42A, 279 (1955).
50. T.Zincke and O.Kegel, Ber., 22, 1467 (1889).
51. T.Zincke and S.Rabinowitsch, Ber., 23, 3766 (1890).
52. J.Stenhouse, Annalen, 163, 174 (1872).
53. T.Zincke and O.Kegel, Ber., 23, 1706 (1890).
54. K.Nierenstein, Chem.Zentr., I, 533 (1906).
55. J.Herzig and F.Wenzel, Monatsh., 27, 784 (1906).
56. K.Kohlrausch, Ber., 69, 527 (1936).
57. A.Lambrechts, Compt.rend., 198, 1852 (1934).
58. N.A.Valuashko and E.M.Voroshin, Trudy Khar'kov.Khim.--Tekhnol.Inst., 5, 15 (1945).
59. T.Campbell and G.Coppinger, J.Amer.Chem.Soc., 73, 2708 (1951).
60. H.Kohler and H.Soheibe, Z.anorg.Chem., 285, 221 (1956).
61. L.V.Smirnov and A.I.Suprunenko, Optika i Spektrosk., 8, 799 (1960).
62. C.Abichandiani and S.Jatkar, J.Indian Inst.Sci., 21A, 417 (1938).
63. R.Highet and T.Batterham, J.Org.Chem., 29, 475 (1964).
64. E.Terry and N.Milas, J.Amer.Chem.Soc., 48, 2647 (1926).
65. W.Mayer and R.Wiess, Angew.Chem., 68, 680 (1956).
66. C.K.Ingold, "Structure and Mechanism in Organic Chemistry" (Translated into Russian), Inostr.Lit., Moscow, 1959, p.138.
67. A.Birch, J.Chem.Soc., 430 (1944).
68. G.Stork and L.Foremann, J.Amer.Chem.Soc., 68, 2172 (1946).

69. K. Fries and K. Schimmelschmidt, Annalen, 484, 245 (1930).
70. E. Müller, "Neuere Anschauungen der organischen Chemie" (Translated into Russian), Inostr. Lit., Moscow, 1960, p. 458.
71. L. Fieser and E. Hershberg, J. Amer. Chem. Soc., 59, 1028 (1937).
72. H. Euler, H. Hasselquist, and A. Glasser, Arkiv Kemi, 7, 583 (1955).
73. K. Nukada and Y. Bansho, Reports Govt. Chem. Ind. Res. Inst., Tokyo, 49, 15 (1954); Chem. Abs., 50, 11 304 (1956).
74. A. Beckwith and W. Waters, J. Chem. Soc., 1001 (1957).
75. J. Bansho and K. Nakada, Bull. Chem. Soc. Japan, 33, 579 (1960).
76. R. Thomson, J. Chem. Soc., 1737 (1950).
77. R. Thomson, J. Chem. Soc., 1237 (1951).
78. D. Bruce and R. Thomson, J. Chem. Soc., 2759 (1952).
79. D. Bruce and R. Thomson, J. Chem. Soc., 1428 (1954).
80. D. Bruce and R. Thomson, J. Chem. Soc., 1089 (1955).
81. A. Madinaveitia and E. Olay, Anales real Soc. espaf. Fís. Quím., 31, 134 (1933); Chem. Abs., 27, 2146 (1933).
82. E. Olay, Rev. Acad. Cienc. Madrid, 32, 384 (1935); Chem. Abs., 30, 2190 (1936).
83. E. Braude, L. Jackmann, and R. Linstead, J. Chem. Soc., 3548 (1954).
84. A. Etienne and G. Bichet, Compt. rend., 229, 1154 (1949).
85. R. Gill and H. Stonehill, J. Chem. Soc., 1857 (1952).
86. K. Zahn and P. Ochwat, Annalen, 462, 72 (1928).
87. A. Weiss and H. Ford, Arch. Biochem., 22, 288 (1949).
88. A. Wheeler and V. Edwards, J. Amer. Chem. Soc., 38, 387 (1916).
89. M. Flett, J. Chem. Soc., 1441 (1948).
90. Yu. B. Shvetsov and M. M. Shemyakin, Zhur. Obshch. Khim., 19, 480 (1949).
91. M. Carmack, M. Moore, and E. Balis, J. Amer. Chem. Soc., 72, 844 (1950).
92. M. Moore and W. Washburn, J. Amer. Chem. Soc., 77, 6384 (1955).
93. L. A. Shchukina, A. S. Khokhlov, and M. M. Shemyakin, Zhur. Obshch. Khim., 21, 908, 1661 (1951).
94. H. Jaffe, J. Amer. Chem. Soc., 77, 4448 (1955).
95. A. Bayer and H. Coro, Ber., 7, 967 (1874).
96. H. Goldsmidt, Ber., 17, 213 (1884).
97. H. Hodgson and F. Moore, J. Chem. Soc., 2499 (1923).
98. H. Hodgson and F. Moore, J. Chem. Soc., 2269 (1925).
99. H. Hodgson and A. Kershaw, J. Chem. Soc., 1555 (1929).
100. H. Hodgson and A. Kershaw, J. Chem. Soc., 967 (1930).
101. H. Hodgson and A. Kershaw, J. Chem. Soc., 1969 (1930).
102. H. Hodgson, J. Chem. Soc., 1494 (1931).
103. H. Hodgson, J. Chem. Soc., 866 (1932).
104. H. Hodgson, J. Chem. Soc., 1392, 1395 (1932).
105. H. Hodgson and D. Nicholson, J. Chem. Soc., 1808 (1939).
106. H. Hodgson, J. Chem. Soc., 89 (1943).
107. W. Hartley, Proc. Chem. Soc., 20, 160 (1904).
108. C. Baly, W. Edwards, and A. Stewart, J. Chem. Soc., 89, 514 (1906).
109. L. Anderson and M. Geiger, J. Amer. Chem. Soc., 54, 3064 (1932).
110. A. Baker, J. Phys. Chem., 62, 744 (1958).
111. H. Hodgson, J. Chem. Soc., 520 (1937).
112. L. Anderson and R. Janke, J. Amer. Chem. Soc., 56, 732 (1934).
113. P. Ramart-Lucas, M. Martynoff, M. Grumez, and M. Chauvin, Bull. Soc. chim. France, 571 (1948).
114. P. Ramart-Lucas and M. Martynoff, Compt. rend., 227, 906 (1948).
115. P. Ramart-Lucas, M. Martynoff, M. Grumez, and M. Chauvin, Bull. Soc. chim. France, 53 (1949).
116. P. Ramart-Lucas, M. Martynoff, and M. Grumez, Bull. Soc. chim. France, 905 (1949).
117. P. Ramart-Lucas, M. Martynoff, M. Grumez, and M. Chauvin, Bull. Soc. chim. France, 901 (1949).
118. M. Green and S. Marcinkiewicz, J. Chromatog., 10, 354 (1963).
119. E. Havinga and A. Schors, Rec. Trav. chim., 69, 457 (1959).
120. W. Vaughan and G. Finch, J. Org. Chem., 21, 1201 (1956).
121. H. Hodgson and D. Nicholson, J. Chem. Soc., 1268 (1940).
122. A. Schors, A. Kraaijeveld, and E. Havinga, Rec. Trav. chim., 76, 490 (1957).
123. M. Baltazzi, Compt. rend., 232, 986 (1951).
124. D. Hadzi, J. Chem. Soc., 2725 (1956).
125. A. N. Nesmeyanov and D. N. Kravtsov, Dokl. Akad. Nauk SSSR, 135, 331 (1960).
126. F. Minisci, R. Calli, and A. Quilico, Tetrahedron Letters, 785 (1963).
127. A. Burawoy, M. Cais, J. Chamberlain, F. Liversedge, and A. Thompson, J. Chem. Soc., 3727 (1955).
128. L. Henrich and V. Eisenach, J. prakt. Chem., [2], 70, 332 (1904).
129. D. Dyrssen and E. Johansson, Acta Chem. Scand., 9, 763 (1955).
130. T. Zincke and N. Bindewald, Ber., 17, 3026 (1884).
131. H. U. Zollinger, "Chemische Reihe, Bd. XIII, Chemie der Azofarbstoffe" (Translated into Russian), Goskhimizdat, Leningrad, 1960.
132. P. Pascal, Ann. Chim. Phys., 25, 372 (1912).
133. A. Hantzch and A. Burawoy, Ber., 63, 1760 (1930).
134. A. Hantzch, Ber., 52, 509 (1919).
135. C. Bury, J. Amer. Chem. Soc., 57, 2116 (1935).
136. E. Eistert, Angew. Chem., 49, 33 (1936).
137. F. Arndt and B. Eistert, Ber., 71, 2040 (1938).
138. R. Kuhn and F. Bar, Annalen, 516, 143 (1925).
139. W. Borshe, W. M. Müller, and C. Bodenstein, Annalen, 472, 201 (1929).
140. W. Lauer and S. Miller, J. Amer. Chem. Soc., 57, 520 (1935).
141. E. Sawicki, J. Org. Chem., 22, 915 (1957).
142. E. Sawicki, J. Org. Chem., 22, 1084 (1957).
143. G. Badger and R. Buttery, J. Chem. Soc., 614 (1956).
144. E. Weiss-Berg and R. Wizinger, Helv. Chim. Acta, 40, 1056 (1957).
145. K. Ueno, J. Amer. Chem. Soc., 79, 3066 (1957).
146. L. Skulski and T. Urbanski, Roczniki Chem., 34, 141 (1960).
147. P. Ramart-Lucas, T. Guilmart, and M. Martynoff, Bull. Soc. chim. France, 75 (1944).
148. A. Burawoy and A. Thompson, J. Chem. Soc., 1443 (1953).
149. D. Hadzi, J. Chem. Soc., 2143 (1956).
150. J. Ospenson, Acta Chem. Scand., 5, 491 (1951).
151. H. Shingu, Sci. Papers Inst. Phys. Chem. Res., Tokyo, 52, 78 (1939).
152. P. Ramart-Lucas, T. Guilmart, and M. Martynoff, Bull. Soc. chim. France, 75 (1944).
153. W. Brode and L. Herdle, J. Org. Chem., 6, 713 (1941).
154. E. Sawicki, J. Org. Chem., 22, 743 (1957).
155. A. Burawoy, A. Salem, and A. Thompson, J. Chem. Soc., 4793 (1952).
156. A. Burawoy, A. Salem, and A. Thompson, J. Chem. Soc., 668 (1952).
157. J. Ospenson, Acta Chem. Scand., 4, 1351 (1951).
158. N. Sidgwick, Ann. Reports, 31, 40 (1934).
159. S. Hendricks, O. Wulf, G. Hibbert, and U. Liddel, J. Amer. Chem. Soc., 58, 1991 (1936).
160. A. Burawoy and J. Chamberlain, J. Chem. Soc., 3734 (1952).
161. J. Rigaudy and L. Nedelec, Bull. Soc. chim. France, 400 (1960).
162. L. Nedelec and J. Rigaudy, Bull. Soc. chim. France, 1204 (1960).

163. E. Bartel and Z. Grabowski, Roczniki Chem., 31, 27 (1957).
164. L. Filar and S. Winstein, Tetrahedron Letters, 6 (1960).
165. C. Cook and B. Norcross, J. Amer. Chem. Soc., 78, 3797 (1956).
166. C. Cook and B. Norcross, J. Amer. Chem. Soc., 81, 1176 (1959).
167. G. A. Nikiforov and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 293 (1964).
168. K. Ley, Angew. Chem., 70, 74 (1958).
169. E. Müller, A. Hubell, H. Suhr, and U. Heilmann, Ber., 95, 638 (1962).
170. L. Cohen, J. Org. Chem., 22, 1333 (1957).
171. E. Müller, R. Mayer, U. Heilmann, and K. Scheffler, Annalen, 645, 66 (1961).
172. G. A. Nikiforov and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 176 (1964).
173. N. A. Vysotskaya, Dokl. Akad. Nauk SSSR, 143, 847 (1962).
174. L. A. Kazitsina, B. S. Kikot', B. V. Rassadin, and O. A. Reutov, Zhur. Obshch. Khim., 33, 223 (1963).
175. V. V. Ershov and G. A. Nikiforov, Dokl. Akad. Nauk SSSR, 158, 1362 (1964).
176. G. A. Nikiforov and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1335 (1964).
177. L. Cohen and W. Jones, J. Amer. Chem. Soc., 85, 3397 (1963).
178. L. Cohen and W. Jones, J. Amer. Chem. Soc., 85, 3402 (1963).
179. A. Hantzsch, Ber., 40, 330 (1907).
180. A. Hantzsch and K. Meisenburg, Ber., 43, 95 (1910).
181. L. Cohen and W. Jones, J. Amer. Chem. Soc., 85, 3397 (1963).
182. A. Hantzsch and U. Gorki, Ber., 39, 1073 (1906).
183. T. Coffield, A. Filbey, G. Ecke, and A. Kolka, J. Amer. Chem. Soc., 79, 5019 (1957).
184. G. A. Nikiforov and K. M. Dyumaev, Izv. Akad. Nauk SSSR, Ser. Khim., 1068 (1964).
185. A. Balaban, M. Gavat, M. Mocanu, and C. Nenitzescu, Rev. Roumaine Chim., 9, 79 (1964).
186. L. Cohen and W. Jones, J. Amer. Chem. Soc., 82, 1907 (1960).
187. L. Cohen and W. Jones, J. Amer. Chem. Soc., 84, 1625 (1962).
188. L. Cohen and W. Jones, J. Amer. Chem. Soc., 84, 1629 (1962).

Institute of Chemical Physics,
Academy of Sciences of the
USSR, Moscow

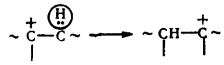
U. D. C. 547.313 : 542.952.6

ANOMALOUS POLYMERISATION OF SOME VINYL MONOMERS

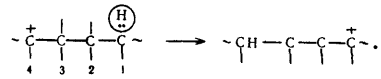
N. D. Prishchepa, Yu. Ya. Gol'dfarb, and B. A. Krentsel'

The problem of the regulation of the chain structure of polymers has always attracted the attention of many investigators. The discovery of stereospecific polymerisation was a great step forward in this direction. One of the interesting possibilities of regulating the chemical structure of macromolecules consists in changing the structure of the monomeric unit during the course of the polymerisation. This process, usually termed conversion or isomerisation polymerisation, results in the growth of the polymeric chain with simultaneous migration of a labile hydrogen atom or group of atoms.

Until now the most characteristic examples of anomalous polymerisation were observed mainly in cationic polymerisations, which are accompanied by the migration of a hydride ion [1]:



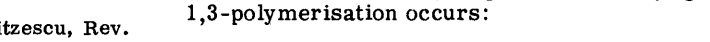
The hydride ion can migrate not only to neighbouring carbon atoms but also to those more distant:



Some authors [2,3] think that the transfer of hydrogen should be sequential: 1–2, 2–3, 3–4, etc.; others [4-6], that the migration takes place directly: 1–3, 1–4, etc.

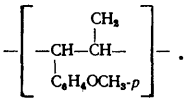
It is noteworthy that hydride transfer reactions have long been known in organic chemistry. Thus, to explain isomerisation, alkylation, cracking, and other reactions, many schemes involving intramolecular or intermolecular migration of hydrogen have been proposed [7-16].

The first suggestions about the possibility of hydrogen migration in polymerisation were made by Staudinger and Dreher [17] in 1935 in studying the polymerisation of β-methylstyrene and acetone. They performed the polymerisation in the presence of tin(IV) chloride and boron trifluoride in toluene at temperatures from 0° to -78° and suggested that polymerisation does not proceed in the usual way but with migration of a labile hydrogen of the methyl group, that is, 1,3-polymerisation occurs:



Ozonation and pyrolysis were used to determine the structure of the polymers. Ozonation did not give results. β-Methylstyrene and acetone, and a little 1,4-diphenylbutadiene and 1,4-di-(*p*-methoxyphenyl)butadiene were detected in the products from pyrolysis at 300°.

The presence of these compounds in the pyrolysis products is attributed to the initial macromolecules having contained structures formed as a result of anomalous polymerisation. Later, a group of Hungarian scientists verified Staudinger and Dreher's results [18]. They polymerised anethole in benzene solution in the presence of tin(IV) chloride and titanium(IV) chloride at room temperature. On investigating the product, they concluded that the polyanethole had the general structure:



On comparing the results of the work of Staudinger and the Hungarian scientists, it is obvious that the conditions of the experiments were not identical; Staudinger carried out the polymerisation at low catalyst concentrations; the Hungarians studied the polymerisation at room temperature with high catalyst concentrations.

Italian scientists investigated the polymerisation of anethole in the presence of aluminium chloride, titanium(IV)