THE REACTIONS OF 8-QUINOLINOL

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I. INTRODUCTION

Of the seven possible quinolinols only 8-quinolinol forms chelate compounds with metal ions. The uses of these chelate compounds for the determination of the metals, particularly magnesium and aluminum, have been the subject of more than five hundred articles since 1927, as well as of several reviews (15, 96, 152, 293). Medicinal and agricultural uses of 8-quinolinol have been investigated in equal detail, starting before 1900 (211), and the fungicidal and bactericidal action of the compound has been attributed in part to its ability to chelate with, and thus inactivate, essential trace metals.

In addition to chelation reactions 8-quinolinol forms salts with both acids and bases and undergoes most of the typical phenol and quinoline reactions. In its phenolic properties (83) it resembles α-naphthol except for some decrease in activity and alteration of products in a few reactions, a difference which is due to its chelating and basic functions.

8-Hydroxyquinoline is the name most frequently used in the analytical literature; the trivial name oxine is very convenient, particularly for the description of the chelate compounds, which may be called oxinates.

This review is concerned only with the chemical reactions of 8-quinolinol and covers the literature through 1954.

II. Reactions of 8-Quinolinol with Metal Ions

Disregarding water of crystallization the normal chelate compounds of 8-quinolinol have the formula $M(C_9H_6NO)_n$, in which n is the valence of the metal ion M. Ions giving normal oxinates include Cu^{+2}, Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Zn^{+2}, Cd^{+2}, Al^{+3}, Ga^{+3}, In^{+3}, Tl^{+3}, Yt^{+3}, La^{+3}, Pb^{+2}, Sb^{+3}, Bi^{+3}, Cr^{+3}, MoO_2^{+2}, Mn^{+2}, Fe^{+3}, Co^{+2}, Ni^{+2}, Pd^{+2}, Ce^{+3}, Pr^{+3}, and several of the other rare earths. Usually only one valence state of an element forms an insoluble, stable chelate compound because of the oxidizing and reducing action of 8-quinolinol itself; for example, ferrous ion can be oxidized to ferric, cerous to ceric, and chromous to chromic, and chromate ion can be reduced to chromic.

The strong tendency for the oxinates to form is shown by the good yields that can be obtained from the direct solution of zinc, copper, and other metals in nitrobenzene–alcohol solutions of 8-quinolinol (306) and in the molten reagent. The stability constants for many of the divalent metal oxinates have been measured in mixtures of dioxane and water (130, 133, 166, 179, 184) and follow, with minor exceptions, the order of decreasing stability that seems to be common to all chelating agents (131): $Pd > Cu > Ni > Co > Zn > Cd > Mn > Mg$. The stabilities are remarkably great (133) as compared to most of the other chelating agents for which data are available, including a number of 8-quinolinol derivatives and structural analogs.

The absorption spectra of the divalent metal oxinates show a bathochromic shift of the principal band of 8-quinolinol that is greatest for the most stable chelates (273). By the same criterion cobaltic and chromic oxinates were judged to be more stable than the aluminum, gallium, indium, and thallic chelates. In most of the metal oxinates the principal absorption band seems to be the 8-quinolinol band in acid solution displaced to longer wavelengths, as might be anticipated for the replacement of hydrogen by elements of greater weight and size (186, 188).

The solubility-product constants of the oxinates as reported by various work-

TABLE 1

Solubility products of metal oxinates

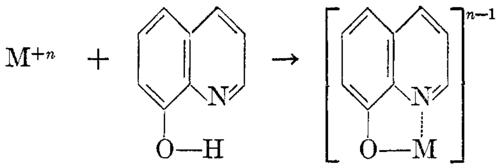
Metal Ion	p*K*	Reference	Metal Ion	p*K*	Reference
Cu^{+2}	29.57	(200)	Ca^{+2}	11.22	(197)
Ni^{+2}	26.05	(199)	Sr^{+2}	9.33	(198)
Co^{+2}	24.77	(199)	Ba^{+2}	8.49	(198)
Zn^{+2}	24.50	(200)	Al^{+3}	32.3	(148)
Pb^{+2}	22.00	(199)	Ga^{+3}	40.8	(148)
Cd^{+2}	21.956	(200)	In^{+3}	36.7	(148)
Mn^{+2}	17.8	(28)	Tl^{+3}	37.2	(28)
Mg^{+2}	15.55	(198)	Fe^{+3}	47	(251)

ers show very unsatisfactory quantitative agreement (18, 28, 148, 197, 198, 199, 200, 227, 286), possibly because much of the work is based on inexact data on the pH of precipitation. Qualitatively, however, the most stable chelate compounds have the lowest solubility in water (table 1) and the solubility of all of them is very low. For many divalent ions thermodynamic solubility-product constants have been calculated and these are probably very reliable; the constants for the trivalent ions can not be considered so reliable: for example, values for the solubility product of ferric oxinate differing by 10^{15} are available in the recent literature.

Thermal stability studies of most of the metal oxinates have been performed with the Chevenard thermobalance (71); some are stable at temperatures as high as 300°C., with cadmium oxinate remaining undecomposed up to 384°C. The majority of the divalent metal oxinates carry two molecules of water at room temperature (27); the degree of hydration at other temperatures and the temperature required to remove water have been the subjects of much conflicting data in the analytical literature.

That residual valence forces exist in the metal oxinates is shown by their ability to add hydrogen chloride (285), one molecule adding to each oxygen and nitrogen; thus, divalent metal oxinates add four molecules and trivalent oxinates six.

Although 8-quinolinol is said to be in the form of a keto tautomer to an extent of about 30 per cent in some solvents (258), the oxinates are not obtained from the keto form (257) but are formed through an electrovalent bond to oxygen and a coördinate bond to nitrogen. The formation proceeds stepwise, one molecule of oxine reacting with the metal ion to give $M(C_9H_6NO)^{n-1}$ (I), followed by reaction with another oxine molecule to give $M(C_9H_6NO)_2^{n-2}$, and so on until a neutral compound is obtained. Sometimes these intermediate ions can be identified in solution or precipitated as basic salts.

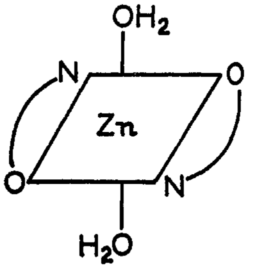


I

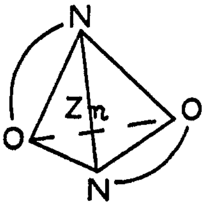
On the basis of stability regularities two classes of divalent metal oxinates have been distinguished (214): those in which the metal ion reacts primarily with the negatively charged oxygen (zinc, cadmium, magnesium) and those in which primary reaction may possibly be with the covalent nitrogen (cobalt, copper, nickel).

In the completed chelate compounds bonding of the metal seems to be predominantly ionic in the magnesium, nickel, and zinc compounds, since these rapidly exchange their metal content with the corresponding ions. Indication of ionic bonding in the copper chelate as well is provided by the coupling of this compound with diazonium salts in an acid solution, a reaction which requires the oxinate ion and therefore occurs with oxine itself only in an alkaline solution (147). Since aluminum oxinate does not couple under similar conditions, the bonds to aluminum may be considered predominantly covalent.

X-ray diffraction studies of zinc oxinate dihydrate have shown (181, 182) a *trans*-planar arrangement of the two oxinate groups about the central zinc atom (II); since the zinc, cadmium, lead, cobalt, copper, and nickel compounds are isomorphous, this same configuration should exist in all. However, the anhydrous zinc oxinate appears to have a tetrahedral zinc atom (III).



II



III

Scandium, thorium, uranium, and plutonium form unusual oxinates containing an added molecule of reagent, as indicated by the formulas $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$, $Th(C_9H_6NO)_4 \cdot C_9H_7NO$, $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$, and $PuO_2(C_9H_6NO)_2 \cdot C_9H_7NO$. This excess reagent is loosely bound, probably by weak lattice forces (189, 238), so that the compounds are stable only in the solid phase and lose the added oxine on heating.

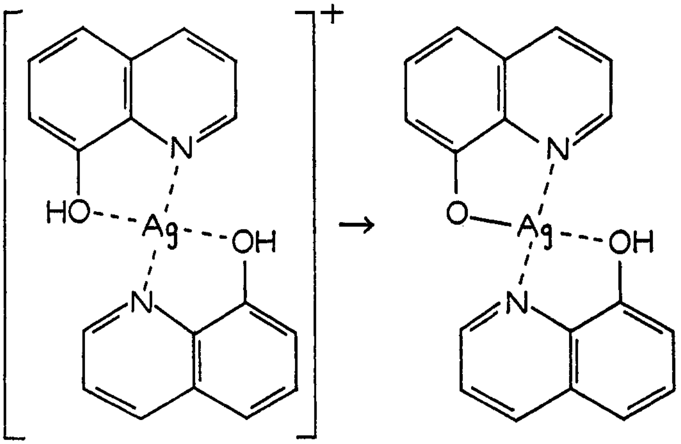
The alkali metals and the thallous ion apparently can not form chelate compounds with oxine but do yield rather insoluble salts from an alkaline solution. Germanium, niobium, tantalum, and several non-metallic elements form complex compounds with 8-quinolinol which have indefinite or inadequately described structures. Mercuric compounds are unique in substituting in the quinoline ring, a reaction characteristic of phenols.

In the following sections the formation of chelate compounds by the individual elements will first be discussed and then the reactions yielding salts or complex compounds other than chelates.

A. CHELATE COMPOUNDS

1. Elements of Group I

Silver nitrate reacts with 8-quinolinol to precipitate a complex compound that is formulated as the nitrate of the ion $[Ag(C_9H_7NO)_2]^{+1}$ (IV), in which all bonds to silver are coördinate. The α-bromo-*d*-camphor-π-sulfonate of this ion has been resolved into optical isomers (124), but neutralization of the salt results in loss of optical activity. Neutralization of the nitrate gives the chelate compound $Ag(C_9H_6NO)(C_9H_7NO)$ (V).



IV V

A reported preparation of an argentic oxinate (202) has been discredited (24), because divalent silver is too strong an oxidizing agent to exist in the conditions specified for the preparation, and even silver acetate can be partially reduced to the metal by 8-quinolinol. The claim that a trivalent silver oxinate (206) was obtained must be considered very questionable.

According to x-ray diffraction studies (142) cupric oxinate dihydrate has a square-planar arrangement of the two oxine residues about the copper, with the molecules of water above and below the plane; it is presumed (142) that the square-planar arrangement would be preserved in the anhydrous oxinate also. Although the magnetic moment of copper oxinate has been measured (242), it offers no conclusive information about bond type; however, ionic bonds are not probable for the square-planar structure.

Gold chelates of 8-quinolinol are apparently unknown; some difficulty in preparing them might be expected because of the reducing properties of oxine.

2. Elements of Group II

All elements of this group except mercury form divalent ion oxinates, all characterized by a yellow fluorescence. Mercuric salts substitute in the 5- and 7-positions of the quinoline ring (see page 284), but the possibility that they also form chelates is not excluded.

The only oxinate of the group that offers difficulties in preparation is the beryllium compound; although the normal oxinate, $Be(C_9H_6NO)_2$, can be prepared (69), it is hard to obtain in a pure condition and is not recommended for use in analysis (96).

Magnesium oxinate is one of a very few magnesium compounds sufficiently stable not to precipitate magnesium hydroxide on boiling with sodium hydroxide, but its magnesium content is rapidly exchanged with magnesium salts, even in a two-phase system, as shown by investigations using radioactive magnesium (248). A similar rapid exchange of zinc in the zinc oxinate (6, 106) is evidence that these chelates have essentially ionic bonds to the metal.

Heating magnesium oxinate at 160°C. for some time is said to produce magnesium oxide and 8,8′-diquinolyl ether (27), but the ether has not been adequately identified and characterized.

3. Elements of Group III

With the exception of boron and scandium all elements of Group III form normal oxinates of the formula $M(C_9H_6NO)_3$. Scandium resembles thorium in forming an oxinate carrying an extra molecule of oxine (236, 237) that is only weakly bound (238). Although no chelate compounds of boron with oxine are known, tetraphenyldiboron oxide (207) and the pyrocatechol–borate complex,

$$C_6H_4O_2BOBO_2C_6H_4$$

form crystalline salts (252).

In addition to the normal thallic oxinate (87, 88, 185) a thallous compound, $Tl(C_9H_6NO)$, probably a salt, can be prepared (185, 244).

4. Lanthanides and actinides

Although all the rare earths have not been tried in reactions with 8-quinolinol, normal oxinates of the trivalent ions appear to be the usual products. Some difficulties in obtaining pure rare earth oxinates seem to be due to their ready hydrolysis. There are indications (133) that the stability of the rare earth oxinate series increases as the inner electrons are filled in.

The stabilization of rare valences of the lanthanides by the formation of oxinates has been attempted, but claims of quadrivalent praseodymium (143, 203) and neodymium (204, 205) chelates are based on incorrect experimental interpretation (241). The preparation of a ceric oxinate, $Ce(C_9H_6NO)_4$, by the addition of 8-quinolinol to a neutral cerous solution (234) is interesting because quadrivalent cerium quantitatively oxidizes oxine in acid solution, while in this reaction 8-quinolinol oxidizes cerium. The oxidation does not take place rapidly, and in the presence of tartrate a cerous oxinate may also be obtained.

Oxinates of the actinides that have been investigated contain added molecules of 8-quinolinol, as shown by the following formulas: $Th(C_9H_6NO)_4 \cdot C_9H_7NO$ (81, 100), $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ (10, 289), and $PuO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ (121). A color change is associated with the loss of the added reagent by heating. By precipitation from a cold solution it is possible to obtain directly the normal thorium oxinate, $Th(C_9H_6NO)_4$. Tracer studies of the distribution of thorium between oxine in water and chloroform show the presence of additional complex compounds (72). The normal oxinate of quadrivalent plutonium, $Pu(C_9H_6NO)_4$, has also been prepared (217).

5. Elements of Group IV

Information about chelate compounds of oxine with Group IV elements is incomplete. The only ion of this group that certainly forms the normal oxinate is divalent lead. This chelate presumably has the *trans*-planar structure with no appreciable dipole moment (44); its position in the stability series for divalent ions is anomalous as compared to lead compounds of other chelating agents (133).

An oxinate of the titanyl ion having the formula $TiO(C_9H_6NO)_2$ has been reported, but it is probably always contaminated with basic compounds such as $TiO(OH)(C_9H_6NO)$ and $Ti(OH)_2(C_9H_6NO)_2$ (27) so that analysis for titanium with oxine is unsatisfactory. Although zirconium is precipitated by 8-quinolinol the product does not correspond to any simple formula and may be considered a mixture of varying proportions of $ZrO(C_9H_6NO)_2$, $Zr(OH)_2(C_9H_6NO)_2$, $ZrO(OH)(C_9H_6NO)$, and $ZrO(OH)_2$ (27).

6. Elements of Group V

Only antimony, bismuth, and vanadium of this group form definite chelate compounds with 8-quinolinol. Trivalent antimony gives the normal oxinate, $Sb(C_9H_6NO)_3$ (235), and esters of antimony compounds with oxine have also been mentioned (65). Bismuth similarly forms a normal oxinate that is useful in analysis (293), as well as the basic compounds $Bi(OH)_2(C_9H_6NO)$ (80) and $Bi(NO_3)(C_9H_6NO)_2$ (62). Bismuth chloride gives a derivative for which the formula $BiCl_3(C_9H_7NO)_2 \cdot 2HCl$ has been written (62); in this compound the bismuth is supposed to be attached by secondary valence forces to the 5- and 7-positions of the two oxine molecules, because a similar compound is obtained from 8-methoxyquinoline but not from 5,7-dibromo-8-quinolinol. It would seem more plausible to consider the compound a salt. In the presence of iodide bismuth compounds give a voluminous red precipitate of the $HBiI_4$ salt of oxine (150).

The reactions of several of the valence states of vanadium with oxine have been studied. In an acid solution vanadates give a black precipitate recently assigned the formula $VO(OH)(C_9H_6NO)_2$ (21, 192) and supposed to be a normal chelate of the ion $VO(OH)^{+2}$. In alkaline solution vanadates give yellow compounds such as $VO(ONa)(C_9H_6NO)_2$, which are salts rather than chelates; on acidification these salts are converted to the black chelate. Two out of six possible geometric isomers of the chelate have been isolated, one violet and corresponding to a *trans-syn-syn* configuration, the other red and having the *trans-anti-anti* configuration (21). Since the violet form is converted to the red in chloroform by alcohols, this reaction is used as a test for alcohols (22, 36) and other color reactions with other functional groups have also been described.

Reduction of $VO(OH)(C_9H_6NO)_2$ with hydrogen over palladium (21) gives the quadrivalent vanadium chelate, $VO(C_9H_6NO)_2$, a compound also obtained from the reaction of vanadyl sulfate with oxine. Further reduction with hydrogen produces the trivalent vanadium compound, $V(OH)(C_9H_6NO)_2$, while the normal oxinate of this valence state, $V(C_9H_6NO)_3$, is formed by the direct reaction of vanadic sulfate with oxine. A vanadous oxinate, stabilized by the addition of two molecules of pyridine, has also been reported (63).

7. Elements of Group VI

Hexavalent molybdenum and tungsten form chelate compounds with oxine having the formulas $MoO_2(C_9H_6NO)_2$ and $WO_2(C_9H_6NO)_2$; the formula of the tungsten compound has been questioned, however (71). Hexavalent chromium is reduced by 8-quinolinol (118) and chromous ion is oxidized (138), so that the only simple chelate compound obtainable is chromic oxinate, $Cr(C_9H_6NO)_3$, and the reported preparation (128) of a chromous oxinate is incorrect (138). Complex ammines of chromium containing one or more oxinate anions have been obtained from reacting the appropriate complex cation with the potassium salt of 8-quinolinol (275), yielding such compounds as $[Cr(NH_3)_6](C_9H_6NO)_3$ and $[Cr[CO(NH_2)_2]_6](C_9H_6NO)_3$.

8. Elements of Group VII

Of this group only the manganous ion has been shown to form the normal oxinate, $Mn(C_9H_6NO)_2$. Heptavalent rhenium is not precipitated by oxine, but an adequate search for possible chelate compounds of the many other valences of this element has not yet been made.

9. Elements of Group VIII

The usual product from reacting either ferrous or ferric solutions in air with 8-quinolinol is the black ferric oxinate, $Fe(C_9H_6NO)_3$, but the intense green of acid solutions of ferric ion and oxine is ascribed to the intermediate ion $Fe(C_9H_6NO)^{+2}$ (251), and the basic salt $FeCl(C_9H_6NO)_2$ is also known (101). Complex ferric compounds such as the fluoride and phosphate are said to give the same color reaction as the free ferric ion; only the ferrocyanide ion is sufficiently stable to give no color (265). A red ferrous oxinate can be prepared (131, 306) but is stable only under reducing conditions (166).

The divalent nickel oxinate, $Ni(C_9H_6NO)_2$, is paramagnetic (183, 299) and exchanges rapidly with nickel ions (119); from this information it is concluded (11) that nickel is tetrahedral in this compound. The oxinate can add three molecules of pyridine to give a paramagnetic compound in which nickel has a coördination number of six, one molecule of the pyridine being regarded as solvent of crystallization (11).

The divalent cobalt oxinate is the only derivative encountered in analytical practice, but a cobaltic oxinate is known (1, 146) as well as complex cobaltic ammines containing oxinate anions (275).

Of the platinum metals palladous ion forms a normal oxinate, $Pd(C_9H_6NO)_2$ (89), as well as an 8-quinolinol salt of the complex acid $H_2Pd(CN)_4$ (90). A trivalent ruthenium derivative has been mentioned (293) but without any details, and apparently no data for the reactions of the other platinum metals exist.

B. SALTS AND COMPLEX COMPOUNDS

The alkali metals form salts in alkaline solution with 8-quinolinol that increase in solubility with increasing atomic weight of the alkali metal (280). The lithium salt has a sufficiently pronounced fluorescence that this property has been suggested for lithium determination (296).

A number of salts of heteropoly acids with 8-quinolinol have been used in gravimetric analysis (30). These include silico- and phosphomolybdates and tungstates and a germanomolybdate; probably the most complex salt of this class for which a formula has been written (165) is $6C_9H_7NO \cdot P_2O_5 \cdot V_2O_5 \cdot 22MoO_3 \cdot xH_2O$.

Arsenic trichloride in ethyl acetate reacts with 8-quinolinol to form a yellow compound, $AsCl_3 \cdot C_9H_7NO$, which is probably a salt (99). Arsenite ion is precipitated by oxine, but the nature of the product has not been elucidated (113).

Niobium and tantalum are precipitated with oxine as complex compounds of uncertain structure containing about 5.5 moles of oxine per mole of the pentavalent metal oxide (293).

Tellurium tetrachloride forms an addition compound with oxine (243).

III. Phenol Reactions

The hydroxyl group of 8-quinolinol is a strong ortho–para-directing influence so that most substituents are introduced in the 5- or 7-position, with the more active electron-seeking reagents substituting in both positions. Generally the 5-position is attacked first. For electron-seeking reagents the influence of the quinoline nitrogen on substituent position is negligible.

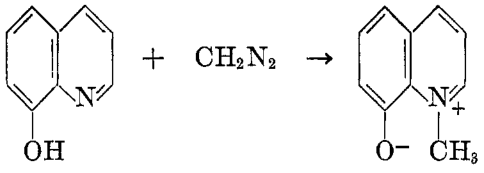
Phenolic reactions requiring metallic catalysts such as zinc and aluminum chlorides are sometimes difficult, since these metals may be chelated and thereby inactivated as catalysts; for example, the Pechmann and Fries reactions have been reported unsuccessful and the Friedel–Crafts reaction gives rather poor results.

A. REACTIONS OF THE HYDROXYL GROUP

1. Ethers and esters

The Williamson ether synthesis using sodium oxinate and an alkyl halide sometimes gives low yields, owing to the formation of quaternary salts of both 8-quinolinol and the ether produced from it. Methyl iodide gives a 12 per cent yield of 8-methoxyquinoline (13, 62, 93, 98), dodecyl bromide 40 per cent of the corresponding ether (144), and ethylene chlorohydrin 19 per cent (37). However, a series of alkyl halides containing from three to eleven carbon atoms gave yields ranging from 50 to 70 per cent (262), and some dihalogenated alkanes can be made to react with two moles of 8-quinolinol (171, 272). In general, alkyl sulfates (93, 135) or alkyl *p*-toluenesulfonates (37) give better yields than the halides. The highest yield obtained by any method is 89 per cent for the β-hydroxyethyl ether, using ethylene carbonate as alkylating agent (39). A vinyl ether has been made from the reaction of oxine with acetylene (86).

The reaction of diazomethane with 8-quinolinol unexpectedly gives only a small amount of 8-methoxyquinoline (40), the principal product being a red, water-soluble compound of structure (VI) somewhat similar to pyocyanine and resulting from the methylation of nitrogen rather than oxygen (223, 253).

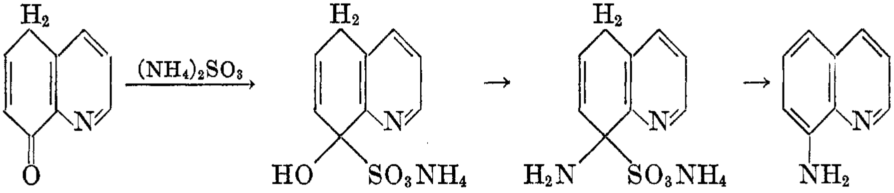


VI

Acid chlorides, both carboxylic (41, 136, 156, 284, 290, 301, 306) and sulfonic (42, 74, 245), give generally excellent yields of 8-quinolinol esters, a few of which are commercially available. Carbamates may also be obtained through reactions of 8-quinolinol with isocyanates (122, 153, 196).

2. Bucherer reactions

A quantitative yield of 8-aminoquinoline results from heating oxine with ammonium sulfite in an autoclave for several hours at 150°C. (303). As indicated by the following reaction sequence, the keto tautomer of oxine is the reactive form.



Zinc chloride ammine and 8-quinolinol heated on an oil bath at 180°C. for 2 hr. also yield 8-aminoquinoline (13). A 37 per cent yield of 8-(*p*-hydroxyphenylamino)quinoline is obtained from *p*-aminophenol, 8-quinolinol, and sodium bisulfite (139). Attempts to obtain a Bucherer type reaction of oxine with hydrazine and hydrazine sulfite did not succeed (7).

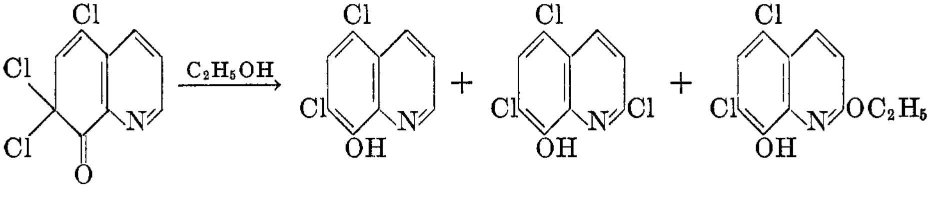
Sodium bisulfite or a solution of sulfur dioxide heated for many hours with oxine gives only a crystalline addition compound of sulfur dioxide that readily loses the sulfur dioxide (302).

B. SUBSTITUTIONS PREDOMINANTLY IN THE 5-POSITION

1. Halogenation and thiocyanation

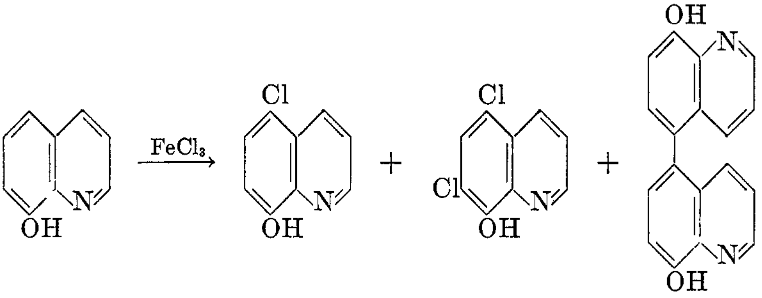
Direct chlorination with one mole of chlorine per mole of oxine gives only a poor yield of 5-chloro-8-quinolinol together with some 5,7-dichloro derivative and unreacted 8-quinolinol (34, 123), but the yield can be increased to 74 per cent by the addition of a little antimony trichloride (250). The use of sulfuryl chloride instead of chlorine has also been proposed (45, 261).

Passing two moles of chlorine into a cooled solution of oxine in acetic acid gives an 85 per cent yield of 5,7-dichloro-8-quinolinol (14, 34, 108, 187); further chlorination produces 5,7,7-trichloro-7,8-dihydro-8-quinolone (VII), which is converted to 5,7-dichloro-8-quinolinol together with small amounts of 2-chloro- and 2-ethoxy-5,7-dichloro-8-quinolinols by warming with ethanol (121). Some 5,6,7-trichloro-8-quinolinol can be recovered from the mother liquor remaining from this exhaustive chlorination.



VII

Ferric chloride reacts with oxine in acid solution to yield as the major product 5,7-dichloro-8-quinolinol together with small amounts of the 5-chloro compound and the oxidation product 8,8′-dihydroxy-5,5′-diquinolyl (VIII) (31). The yield of the latter compound can be increased by conducting the reaction in alkaline solution.



VIII

Sulfur monochloride and dichloride also produce mainly 5,7-dichloro-8-quinolinol (76, 77).

Bromination, like chlorination, gives only a poor yield of the 5-halo derivative (53) if one mole of bromine is used, but a quantitative yield of 5,7-dibromo-8-quinolinol with two moles of bromine (17, 53, 115, 117, 149, 162). This reaction is the basis of a well-known method for the quantitative determination of metals by titrating their oxine equivalent with standard bromate-bromide solution in an acidic medium (293). Bromination with carbonyl bromide also gives the 5,7-dibromo derivative (246).

Direct iodination gives a 40 per cent yield of 5-iodo-8-quinolinol with the 5,7-diiodo compound as a byproduct (162, 173) when one mole of iodine is used per mole of oxine, and iodine monochloride as iodinating agent also gives a rather poor yield of the 5-iodo derivative (108, 111). Reports of the isolation of geometric isomers of monoiodinated oxine (232, 233) cannot be correct.

The use of two moles of iodine monochloride per mole of oxine gives a nearly quantitative yield of 5,7-diiodo-8-quinolinol (61, 64, 107, 111, 215) in a state of purity superior to the product obtained with iodine (49, 173, 216, 268, 305). Electrolysis of an alkaline solution of oxine and potassium iodide also gives this compound (33). The stability of the diiodo derivative cannot be very great, since sodium thiosulfate is capable of removing some of the iodine (70).

A mixture of iodine and chlorine, presumably iodine trichloride, reacts with oxine to form 5-chloro-7-iodo-8-quinolinol (25, 195), which disproportionates on heating in various solvents to an equimolar mixture of 5,7-dichloro-8-quinolinol and 5,7-diiodo-8-quinolinol (210).

Fluorination of oxine in the 5-position is effected by diazotization of 5-amino-8-quinolinol and reaction with fluoboric acid (125, 126).

Although the halogens substitute in both the 5- and the 7-position even when one mole is used per mole of 8-quinolinol, only monosubstitution has been observed with the pseudohalogen thiocyanogen (91, 137, 180, 213). By analogy with the behavior of quinoline the thiocyano group was first assumed to be in the 4-position (137), but the compound has been shown to be the 5-thiocyano-8-quinolinol by synthesis from 5-amino-8-quinolinol via the Sandmeyer reaction with cuprous thiocyanate (91).

By boiling the 5-thiocyano compound with potassium hydroxide in air the disulfide is produced (91).

2. Sulfonation and nitration

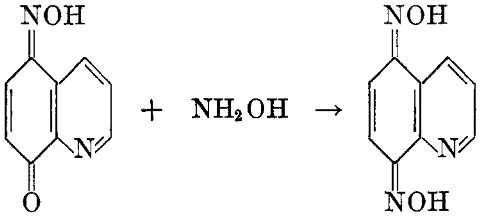
A quantitative yield of 8-hydroxy-5-quinolinesulfonic acid is obtained by the action of fuming sulfuric acid on oxine at 0°C. (57, 173), and the same product results from the reaction of these reagents in a sealed tube at 180°C. (160). Although concentrated sulfuric acid at 100°C. has been claimed to give the 7-sulfonic acid (102, 212), it is probable that this product is also the 5-sulfonic acid derivative (190). More drastic sulfonation conditions using hot fuming sulfuric acid give the 5,7-disulfonic acid; however, two slightly different methods of preparing this compound gave products of differing properties (57, 160).

Direct nitration of oxine can not be controlled to give the 5-nitro derivative, only 5,7-dinitro-8-quinolinol being isolated. A 37 per cent nitric acid solution gives a 57 per cent yield of this compound at room temperatures (267) and other concentrations and conditions (12, 50, 51, 62, 67, 276), if not too drastic, give only this product. More drastic conditions can produce good yields of quinolinic and nicotinic acids.

A convenient route to 5-nitro-8-quinolinol is oxidation of the 5-nitroso compound with nitric acid or hydrogen peroxide (109, 140).

3. Nitrosation

Nitrous acid reacts with 8-quinolinol to give a nearly quantitative yield of 5-nitroso-8-quinolinol (58, 125, 140), a valuable intermediate for the synthesis of other 5-substituted oxines (3) since it can be easily reduced to 5-amino-8-quinolinol, a reactive aromatic amine. The existence of a keto-oxime tautomer of 5-nitroso-8-quinolinol is demonstrated by its reaction with hydroxylamine to form 5,8-quinolinequinone dioxime (IX) (141).


IX

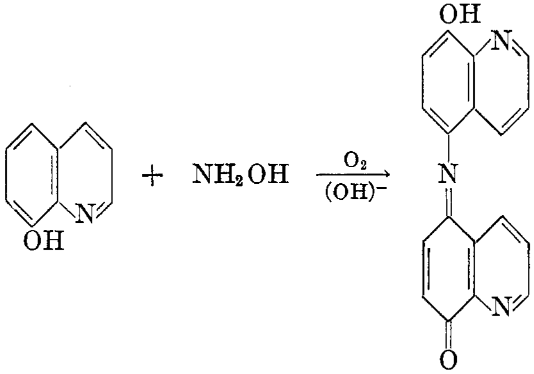
4. Coupling reactions with diazonium compounds

Very good yields of dyes, most of them red or red-brown, are obtained by coupling diazotized amines with 8-quinolinol in an alkaline solution. Rubbing solid oxine with *p*-nitroaniline, sodium nitrite, and potassium bisulfate is even sufficient to produce the reaction (145). The following substituted anilines have been coupled with oxine (46, 97, 114, 116, 172, 174, 264): *o*-, *m*-, and *p*-methylaniline; *o*-, *m*-, and *p*-chloroaniline; *o*-, *m*-, and *p*-nitroaniline; *o*-, *m*-, and *p*-hydroxyaniline; *p*-methoxyaniline; *p*-ethoxyaniline; *p*-bromoaniline; *p*-acetamidoaniline; aniline-*o*-carboxylic acid; *m*- and *p*-anilinesulfonic acids (95); aniline-*p*-arsonic acid (20); *p*-sulfonamidoaniline (85, 300); 2,5-dichloroaniline; 2,6-dimethylaniline; 2-methylaniline-4-sulfonic acid; 5-chloroaniline-2-sulfonic acid. A few heterocyclic amines (163), substituted naphthylamines and benzidines (307, 308) have also been used. Since compounds containing two or three diazotized amino groups can couple more than once, a series of bisazo (4, 48, 249) and trisazo (47, 73, 120, 297) dyes of which oxine provides one component is known.

The only instance of disubstitution of oxine in the coupling reaction is the formation of 5,7-bis(phenylazo)-8-quinolinol (174) from a concentrated solution of diazotized aniline and 8-quinolinol; in more dilute solution only the 5-phenylazo derivative is obtained.

5. Indophenols and indoanilines

Oxidation with potassium dichromate of a mixture of *N*,*N*-dimethyl-*p*-phenylenediamine and 8-quinolinol yields a blue indoaniline (209), and a similar


X

compound is obtained from 4-aminoantipyrine using potassium ferricyanide as oxidant (79, 178). Air oxidation of hydroxylamine and oxine in an alkaline solution gives the blue indophenol (X), presumably formed through 5-amino-8-quinolinol as an intermediate (16, 221). This interpretation has been confirmed by the preparation of the indophenol from 5-amino-8-quinolinol (240).

6. Friedel–Crafts reactions

Since it forms salts with acids and a chelate compound with aluminum, 8-quinolinol should be relatively inactive toward Friedel–Crafts acylation, and early workers did report unsuccessful efforts (98). The Fries rearrangement of 8-acetoxyquinoline also could not be accomplished (29). However, longer reaction times (12 hr.) and elevated temperatures with aluminum chloride as catalyst have produced acylations in moderate yields, as shown by the following examples: a 45 per cent yield of 5-acetyl-8-quinolinol (175, 247), a 17 per cent yield of 5-pelargonyl-8-quinolinol (75), and a 77 per cent yield of 5-benzoyl-8-quinolinol (155, 175).

Phthaloyl chloride has been reported to react with oxine in the presence of aluminum chloride to give 7-*o*-carboxybenzoyl-8-quinolinol with 8,8′-dihydroxydiquinolylphthalide as a side product (176). 7-*o*-Carboxybenzoyl-8-quinolinol is remarkably unstable, decomposing on distillation into phthalic anhydride and oxine and undergoing bromination to 5,7-dibromo-8-quinolinol.

Friedel–Crafts alkylations of 8-quinolinol are unknown.

7. Mercuration

Because oxine is a chelating agent as well as a phenol, some uncertainty about the structures of its mercury derivatives exists (201, 285, 298). However, mercuric acetate yields 5-acetoxymercuri-8-quinolinol (259) and, when an excess of mercuric acetate is used, 5,7-bis(acetoxymercuri)-8-quinolinol (230, 276). 5-Acetoxymercuri-8-quinolinol is converted to the corresponding chloromercuri and hydroxymercuri derivatives by hydrochloric acid and sodium hydroxide, respectively.

In alcohol solution mercuric chloride reacts with oxine to form the compound $Hg_2Cl_3(C_9H_6NO)(C_9H_7NO)$ in which the mercury must be attached to the 5- or 7-position, since 8-methoxyquinoline gives a similar compound but 5,7-dibromo-8-quinolinol does not (62). On heating with hydrochloric acid this compound is converted to $HgCl_2 \cdot C_9H_7NO \cdot HCl$ (62, 298), apparently an addition compound of mercuric chloride and 8-quinolinol hydrochloride.

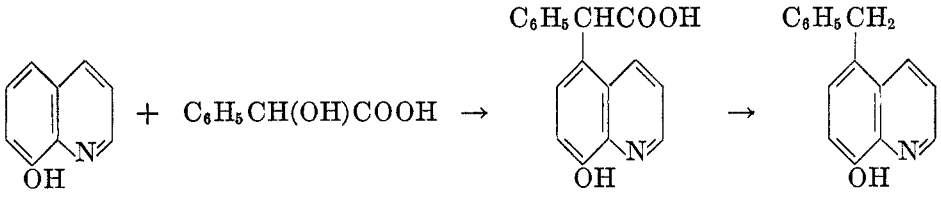
Mercuric nitrate also substitutes in the 5-position (191).

8. Other reactions

The Reimer–Tiemann reaction of oxine with carbon tetrachloride and potassium hydroxide gives a 20–25 per cent yield of 8-hydroxyquinoline-5-carboxylic acid at best (157, 177, 208), but results are erratic. Chloroform in this reaction is said to produce both 8-hydroxyquinoline-5-aldehyde and 8-hydroxyquinoline-7-aldehyde (260).

The Elbs oxidation of 8-quinolinol with potassium persulfate gives only a poor yield of 5,8-quinolinediol (59) because the product is itself sensitive to oxidation to 5,8-quinolinequinone and further decomposition. 5,8-Quinolinequinone, more readily available from other reactions, can be reduced to 5,8-quinolinediol and is converted to 5,6,8-triacetoxyquinoline by acetic anhydride (239).

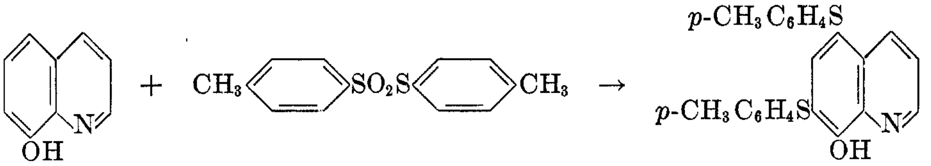
Mandelic acid with 8-quinolinol in concentrated sulfuric acid splits out a molecule of water to form the 5-phenylacetic acid derivative (XI), which is decarboxylated at 170–180°C. to 5-benzyl-8-quinolinol (5).



XI

In a reaction at least superficially similar xanthydrol in acetic acid forms 5-(9-xanthyl)-8-quinolinol (193).

In the presence of sodium ethoxide "*p*-tolyldisulfoxide" reacts with oxine to yield 5,7-bis(*p*-tolylmercapto)-8-quinolinol (XII) (32).



XII

C. SUBSTITUTIONS PREDOMINANTLY IN THE 7-POSITION

If the 5-position of 8-quinolinol is blocked, most of the reactions so far described will yield 7-substituted oxines after removal of the blocking group. Although this technique is the obvious route to many 7-substituted derivatives, it is not considered within the scope of this review.

1. Kolbe reactions

Carbon dioxide at 150°C. under pressure reacts with sodium oxinate to give a quantitative yield of 8-hydroxyquinoline-7-carboxylic acid (254). Esters of this acid with aliphatic alcohols have been prepared (78) and the hydroxamic acid obtained from the reaction of the methyl ester with hydroxylamine.

A similar reaction with potassium ethyl xanthate in place of carbon dioxide gives the 7-dithionic acid, which is converted to the 7-carboxylic acid by potassium hydroxide (158).

2. Condensations with aldehydes

The reaction of formaldehyde with oxine goes easily in both acidic and alkaline media, producing eventually polymers of low molecular weight, although several definite compounds have also been isolated. From a basic solution under the conditions of the Lederer–Manasse reaction an alcohol, $C_9H_6NO(CH_2OH)$, in which the location of the hydroxymethyl group was not specified but is probably 5 or 7, and a formaldehyde addition product of this alcohol have been obtained (167, 168). With more formaldehyde and more drastic conditions a different product is obtained for which no acceptable structure has been proposed; air oxidation of the reaction mixture or ferricyanide oxidation of the isolated product produces a green substance (58), apparently an indication that a di- or triquinolylmethane was present. In sulfuric acid formaldehyde gives a 50 per cent yield of a bis(8-hydroxyquinolyl)methane (209, 256), probably with the linkages to the formaldehyde carbon atom at the 5-positions.

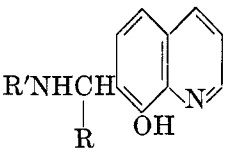
Chloromethylation of oxine with formaldehyde and hydrogen chloride gives a compound of unspecified structure (269, 270), probably 7-chloromethyl-8-quinolinol.

Condensations of oxine with benzaldehyde or other aromatic aldehydes in phosphoric acid have been reported to yield 7-benzal-7,8-dihydro-8-quinolone or derivatives (104). Chloral hydrate in concentrated sulfuric acid gives the compounds 1,1,1-trichloro-2,2-bis(8-hydroxy-*x*-quinolyl)ethane and 1,1,1-trichloro-2-hydroxy-2-(8-hydroxy-*x*-quinolyl)ethane (43), in which *x* is either 5 or 7.

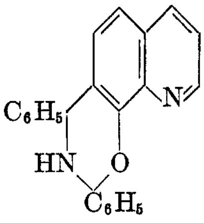
3. Mannich reactions

Secondary amines, formaldehyde, and 8-quinolinol yield 7-aminomethyl oxines; the only secondary amines that have been employed in this reaction are piperidine, dimethylamine, and diethylamine (35, 222).

A similar reaction (Betti reaction), in which formaldehyde is replaced by aromatic aldehydes and secondary amines by primary aromatic or heterocyclic amines, has been used to make a number of 7-substituted oxines of the general formula XIII with R and R′ aryl or heterocyclic groups (224, 225, 231). The reaction appears to be a general one and similar to the condensations of carbonyl compounds with active methylene groups. In some instances cyclization to yield oxazine derivatives may occur; for example, ammonia and two moles of benzaldehyde per mole of oxine form the oxazine (XIV), and amides (rather than amines) with benzaldehyde give similar cyclic compounds (228, 229).



XIII



XIV

4. Claisen reactions

8-Allyloxyquinoline can be prepared in 72 per cent yield from potassium oxinate and allyl bromide (161, 169). On heating to about 200°C. this ether undergoes the Claisen rearrangement to give an 89 per cent yield of 7-allyl-8-quinolinol (38, 161, 169), which may be put through the reaction again to produce 5,7-diallyl-8-quinolinol (169).

By the action of benzyl chloride and sodium hydride on oxine a Claisen type reaction gives a 58 per cent yield of 7-benzyl-8-quinolinol (294, 295).

D. MISCELLANEOUS PHENOL REACTIONS

Pechmann reactions of 8-quinolinol with acetoacetic ester and similar compounds have been reported (2), but later work showed that only a zinc chelate of oxine was actually obtained with zinc chloride as the catalyst and that no products were obtained with other catalysts (288).

Isatin condenses with two moles of 8-quinolinol in the presence of phosphorus oxychloride to yield 2-keto-3,3-bis(8-quinolyloxy)indoline (105, 282).

IV. Quinoline Reactions

A. OXIDATION

The presence of the hydroxyl group makes 8-quinolinol far more sensitive to oxidation than quinoline itself. Oxidation with nitric acid proceeds through the 5,7-dinitro derivative to a 62 per cent yield of quinolinic acid (23, 278), and under drastic conditions for the process it is possible to decarboxylate the quinolinic acid to nicotinic acid (26, 267). Ozone as oxidant in place of nitric acid gives a 90 per cent yield of quinolinic acid (154), but permanganate oxidation gives a rather poor yield (94) in spite of the fact that this oxidation has been suggested as a quantitative method for oxine determination (226). Oxidation with selenium oxychloride and sulfuric acid gives nicotinic acid (194).

Treatment of 8-quinolinol with peracetic (219), perbenzoic (82, 263), or perphthalic acid (218) produces the 1-oxide. The reactivity of this compound offers several possibilities for the synthesis of new oxine derivatives. It is converted by acetic anhydride to a good yield of 2,8-quinolinediol after hydrolysis of the acetate (219).

The heat of combustion of oxine has been measured (281).

B. REDUCTION

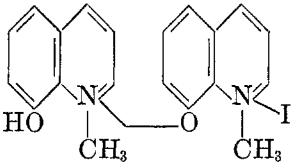
Catalytic hydrogenation over palladium at 55°C. yields 1,2,3,4-tetrahydro-8-quinolinol (41), also obtained by reduction with tin and hydrochloric acid (12) and by electrolysis in acid solution (79 per cent yield) and in basic solution (95 per cent yield) (283).

Polarographic reduction at the mercury cathode (92, 277) shows that 1,4-dihydro-8-quinolinol is probably the initial product in acid solutions and is an intermediate in the reduction to the tetrahydro compound in neutral solution. In alkaline solution a monohydrogenated free radical is postulated as the initial reduction product.

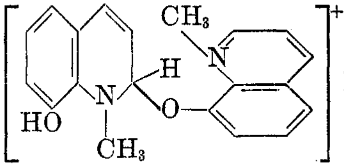
Reduction to 8-hydroxydecahydroquinoline in acetic acid at 45°C. over platinum black gives two isomers, both described as *cis* forms, as well as a small amount of decahydroquinoline (103). Either of the two isomers could be converted to a third, which could be resolved into two optically active forms.

C. QUATERNARY COMPOUNDS

A sealed-tube reaction of methyl iodide with 8-quinolinol produces 8-hydroxy-1-methylquinolinium iodide (52, 159), which can be converted to the hydroxide by silver oxide or excess potassium hydroxide (54). Treatment of the iodide with half a mole of potassium hydroxide gives an intermediate compound that reacts with methyl iodide to form 8-methoxy-1-methylquinolinium iodide and 8-hydroxy-1-methylquinolinium iodide (52). The formula of the intermediate compound as given by Claus (XV) is not acceptable by modern valence theory; however, the compound can be formulated (XVI) as an ether of the pseudo-base form of 8-hydroxy-1-methylquinolinium hydroxide, which might plausibly be formed under these conditions.



XV



XVI

Heating 8-hydroxy-1-methylquinolinium hydroxide in air to 70–80°C. produces the "anhydride" (56), probably the same substance formed by the action of diazomethane on oxine.

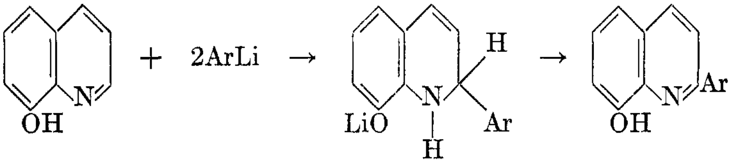
Quaternary compounds with other alkyl halides have been made by similar reactions (55, 304), the most easily prepared coming from phenacyl halides which may react after only 30 min. at 100°C. (8, 9). A silicon-containing quaternary salt, $[(C_9H_7NO)Si(CH_3)_3]Cl$, has been reported (274).

D. SUBSTITUTION IN THE 2-POSITION

Quinoline is reactive at the 2- and 4-positions toward nucleophilic reagents and similar behavior may be expected from 8-quinolinol. However, only substitutions in the 2-position have been effected to date, with no direct substitutions at either the 3- or the 4-position apparently known.

Fusion of oxine with sodium hydroxide gives a poor yield of 2,8-quinolinediol (66); further heating produces a trihydroxyquinoline in which the location of the hydroxyl group is not known. A similar reaction with sodium amide yields 2-amino-8-quinolinol (255), but sodium amide in liquid ammonia at temperatures up to 110°C. will not produce amination (19).

The addition of aryl lithium compounds to 8-quinolinol gives fairly good yields of 2-aryl-8-quinolinols (110, 129, 220). In these reactions an extra mole of the organolithium compound is consumed in reaction with the hydroxyl group. The reactions probably go through a 1,2-dihydroquinoline intermediate (XVII), which is oxidized to the final product. The only example of an alkyl lithium in this reaction is the production in 37 per cent yield of 8-hydroxyquinaldine from methyllithium (287).



XVII

From a consideration of their low reactivity toward quinoline Grignard reagents would not be expected to substitute satisfactorily for lithium compounds in these reactions.

E. SALTS WITH ACIDS

As an organic base 8-quinolinol forms a large number of salts with strong and moderately weak acids, including hydrochloric, phosphoric, thiocyanic, citric, tartaric, succinic, and chloroplatinic. In addition to the isolated salts there is physicochemical evidence for the existence in solution of oxine compounds with acetic, chloroacetic, and benzoic acids (68). Double salts of 8-quinolinol are also known (271). The sulfuric acid salt, $(C_9H_7NO)_2 \cdot H_2SO_4$, has been used for medicinal and agricultural purposes under various trade names, of which the most frequently mentioned is quinosol or chinosol. (This name has also been applied to the potassium bisulfate salt.)

Adducts of 8-quinolinol with picric acid, styphnic acid (127), 1,3,5-trinitrobenzene (279), and 2,4,7-trinitrofluorenone (151) have been suggested as derivatives for characterization.

V. Preparation of 8-Quinolinol

Although this review is limited to the reactions of 8-quinolinol, methods of preparing the compound may be mentioned. Yields from the Skraup reaction of *o*-aminophenol, *o*-nitrophenol, glycerol, and sulfuric acid are poor (132, 266, 292), although better than 90 per cent yields can be obtained from modern modifications in which most of the sulfuric acid is replaced by acetic acid (60) and ferrous sulfate–boric acid additions are used (134, 170). The fusion of 8-quinolinesulfonic acid, obtained by sulfonating quinoline, with sodium hydroxide gives 90 per cent yields (112, 164, 302). Heating 8-chloroquinoline with sodium hydroxide under pressure produces an 87 per cent yield (291), and almost quantitative yields of 8-quinolinol are obtained when 8-aminoquinoline is heated with sulfuric acid in an autoclave (84).

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VI. References

(1) Ablov, A.: Bull. soc. chim. **53**, 234 (1933).
(2) Ahuja, D. P., Chakravarti, K. K., and Siddiqui, S.: J. Sci. Ind. Research (India) **9B**, 187 (1950); Chem. Abstracts **45**, 7125 (1951).

(3) Albert, A., and Magrath, D.: Biochem. J. **41,** 534 (1947).

(4) Anderau, W.: U. S. patent 2,411,646 (1946); Chem. Abstracts **41,** 1455 (1947).

(5) Arventi, B. I.: Ann. sci. univ. Jassy, Pt. I, **23,** 344 (1937); Chem. Abstracts **32,** 5838 (1938).

(6) Atkins, D. C., and Garner, C. S.: J. Am. Chem. Soc. **74,** 3527 (1952).

(7) Badger, G. M., and Buttery, R. G.: J. Chem. Soc. **1955,** 2817.

(8) Bahner, C. T., and Stump, B. L.: J. Am. Chem. Soc. **74,** 3454 (1952).

(9) Bahner, C. T., Walker, L. A., Pierce, F., and Kite, E.: J. Am. Chem. Soc. **73,** 4011 (1951).

(10) Bailar, J. C.: *Inorganic Syntheses*, Vol. IV, p. 101. McGraw-Hill Book Company, Inc., New York (1953).

(11) Basalo, F., and Matoush, W. R.: J. Am. Chem. Soc. **75,** 5663 (1953).

(12) Bedall, C., and Fischer, O.: Ber. **14,** 1368 (1881).

(13) Bedall, C., and Fischer, O.: Ber. **14,** 2570 (1881).

(14) Berg, R.: Z. anorg. allgem. Chem. **204,** 212 (1932).

(15) Berg, R.: *Die analytische Verwendung von o-Oxychinolin und seiner Derivate.* F. Enke Verlag, Stuttgart (1938).

(16) Berg, R., and Becker, E.: Ber. **73B,** 172 (1940).

(17) Berg, R., and Küstenmacher, H.: Z. anorg. allgem. Chem. **204,** 215 (1932).

(18) Berges, L. S.: Anales real soc. españ. fís. y quím. (Madrid) **49B,** 417 (1953); Chem. Abstracts **48,** 1204 (1954).

(19) Bergstrom, F. W.: J. Org. Chem. **3,** 233 (1938).

(20) Berlingozzi, S.: Ann. chim. applicata **18,** 31 (1928); Chem. Abstracts **22,** 1976 (1928).

(21) Bielig, H. J., and Bayer, E.: Ann. **584,** 96 (1953).

(22) Blair, A. J., and Pantony, D. A.: Anal. Chim. Acta **13,** 1 (1955).

(23) Blicke, F. F., and Jenner, E. L.: J. Am. Chem. Soc. **64,** 1722 (1942).

(24) Block, B. P., Bailar, J. C., and Pearce, D. W.: J. Am. Chem. Soc. **73,** 4971 (1951).

(25) Boedecker, F., and Cassel, L.: German patent 697,731 (1938); Chem. Abstracts **35,** 6603 (1941).

(26) Boedecker, F., and Heymons, A.: German patent 817,910 (1951); Chem. Abstracts **47,** 5453 (1953).

(27) Borrel, M., and Paris, R.: Anal. Chim. Acta **4,** 267 (1950).

(27) Borrel, M., and Paris, R.: Anal. Chim. Acta **6,** 389 (1952).

(29) Borsche, W., and Groth, H.: Ann. **549,** 238 (1941).

(30) Brabson, J. A., Mattraw, H. C., Maxwell, G. E., Darrow, A., and Needham, M. F.: Anal. Chem. **20,** 504 (1948).

(31) Bratz, L. T., and von Niementowski, S.: S. Ber. **52,** 190 (1919).

(32) Brooker, L. G. S., and Smiles, S.: J. Chem. Soc. **1926,** 1723.

(33) Brown, O., and Berkowitz, B.: Trans. Electrochem. Soc. **75,** (preprint) 7 pp. (1939).

(34) Buchi, J., and Meier, P.: Acta Pharm. Intern. **2,** 149 (1951); Chem. Abstracts **48,** 12110 (1954).

(35) Burckhalter, J. H., Tendick, F. H., Jones, E. M., Holcomb, W. F., and Rawlins, A. L.: J. Am. Chem. Soc. **68,** 1894 (1946).

(36) Buscarons, F., Marin, J. L., and Claver, J. J.: Anales real soc. españ. fís. y quím. (Madrid) **49B,** 367 (1953); Chem. Abstracts **48,** 80 (1954).

(37) Butler, C. L., and Renfrew, A. G.: J. Am. Chem. Soc. **60,** 1582 (1938).

(38) Buu-Hoï, Ng. Ph., Ki-Wei, H., and Royer, R.: Bull. soc. chim. **12,** 866 (1945).

(39) Carlson, W. W., and Cretcher, L. H.: J. Am. Chem. Soc. **69,** 1956 (1947).

(40) Caronna, G., and Sansone, B.: Gazz. chim. ital. **69,** 24 (1939).

(41) Cavallito, C. J., and Haskell, T. H.: J. Am. Chem. Soc. **66,** 1168 (1944).

(42) Cavallito, C. J., and Haskell, T. H.: J. Am. Chem. Soc. **66,** 1927 (1944).

(43) Chakravarti, K. K.: J. Sci. Ind. Research (India) **9B,** 305 (1950); Chem. Abstracts **45,** 9059 (1951).

(44) Charles, R. G., and Freiser, H.: J. Am. Chem. Soc. **73,** 5223 (1951).

(45) Chinosolfabrik A.-G.: German patent 543,789 (1930); Chem. Abstracts **26,** 3266 (1932).
(46) CIBA, Ltd.: Swiss patent 251,583 (1948); Chem. Abstracts **44,** 6139 (1950).
(47) CIBA, Ltd.: British patent 695,330 (1953); Chem. Abstracts **48,** 4847 (1954).
(48) CIBA, Ltd.: British patent 710,734 (1954); Chem. Abstracts **48,** 24223 (1954).
(49) Claus, A.: German patent 78,880 (1898); Frdl. **4,** 1144.
(50) Claus, A., and Baumann, S.: J. prakt. Chem. [2] **55,** 473 (1897).
(51) Claus, A., and Dewitz, E.: J. prakt. Chem. [2] **53,** 532 (1896).
(52) Claus, A., and Howitz, H.: J. prakt. Chem. [2] **42,** 224 (1890).
(53) Claus, A., and Howitz, H.: J. prakt. Chem. [2] **44,** 444 (1891).
(54) Claus, A., and Howitz, H.: J. prakt. Chem. [2] **45,** 255 (1892).
(55) Claus, A., and Howitz, H.: J. prakt. Chem. [2] **47,** 426 (1893).
(56) Claus, A., and Mohl, E.: J. prakt. Chem. [2] **54,** 6 (1896).
(57) Claus, A., and Posselt, M.: J. prakt. Chem. [2] **41,** 33 (1890).
(58) Cohn, G.: J. prakt. Chem. [2] **83,** 498 (1910).
(59) Dalvi, V. J., Desai, R. B., and Sethna, S.: J. Indian Chem. Soc. **28,** 366 (1951); Chem. Abstracts **47,** 7493 (1953).
(60) Das, A., and Mukherjee, S. L.: Science and Culture (India) **16,** 477 (1951); Chem. Abstracts **46,** 2545 (1952).
(61) David, Ltd.: Indian patent 43,579 (1951); Chem. Abstracts **46,** 7128 (1952).
(62) Dede, L., and Hessler, W.: Z. anorg. allgem. Chem. **188,** 325 (1930).
(63) Dehnert, J.: Dissertation, Jena (1952).
(64) Delaby, R., and Charonnat, R.: IX Congr. intern. quim. pura aplicada **4,** 301 (1934); Chem. Abstracts **30,** 4497 (1936).
(65) Denayer, M.: 15me Congr. chim. ind. (Bruxelles, Sept. 1935) **1936,** 387; Chem. Abstracts **30,** 5582 (1936).
(66) Diamant, M.: Monatsh. **16,** 761 (1895).
(67) Dikshoorn, R. P.: Rec. trav. chim. **48,** 550 (1929).
(68) Dionis'ev, D. E., and Dzhelomanova, Z. K.: Zhur. Obshcheĭ Khim. **24,** 88 (1954); Chem. Abstracts **49,** 3192 (1955).
(69) Dupuis, T.: Mikrochemie ver. Mikrochim. Acta **35,** 477 (1950).
(70) Dupuis, T.: Anal. Chim. Acta **4,** 650 (1950).
(71) Duval, C.: *Inorganic Thermogravimetric Analysis.* Elsevier Publishing Company, New York (1953).
(72) Dyrssen, D.: Svensk. Kem. Tid. **65,** 43 (1953); Chem. Abstracts **47,** 10968 (1953).
(73) Ebert, J.: U. S. patent 1,979,678 (1934); Chem. Abstracts **29,** 1585 (1935).
(74) Ebert, J.: U. S. patent 2,107,856 (1938); Chem. Abstracts **32,** 2692 (1938).
(75) Edgerton, W. H., and Burckhalter, J. H.: J. Am. Chem. Soc. **74,** 5209 (1952).
(76) Edinger, A.: Ber. **30,** 2418 (1897).
(77) Edinger, A.: J. prakt. Chem. [2] **56,** 282 (1897).
(78) Einhorn, A.: Ann. **311,** 64 (1900).
(79) Emerson, E., and Kelley, K.: J. Org. Chem. **13,** 532 (1948).
(80) Engels, W. H.: U. S. patent 1,485,380 (1924); Chem. Abstracts **18,** 1367 (1924).
(81) Eswaranarayana, N., and Raghava Rao, B.S.V.: Anal. Chim. Acta **11,** 339 (1954).
(82) Evans, R. L., and Linsker, F.: U. S. patent 2,518,130 (1950); Chem. Abstracts **45,** 1169 (1951).
(83) Ewing, G. W., and Steck, E. F.: J. Am. Chem. Soc. **68,** 2181 (1946).
(84) Farbenindustrie, I. G.: German patent 485,315 (1926); Chem. Abstracts **24,** 862 (1936).
(85) Farbenindustrie, I. G.: French patent 766,081 (1934); Chem. Abstracts **28,** 7431 (1934).
(86) Farbenindustrie, I. G.: British patent 443,978 (1936); Chem. Abstracts **30,** 5237 (1936).
(87) Feigl, F.: Nature **161,** 436 (1948).

(88) Feigl, F., and Baumfield, L.: Anal. Chim. Acta **3,** 83 (1949).
(89) Feigl, F., and Feigl, H. E.: Anal. Chim. Acta **3,** 300 (1949).
(90) Feigl, F., and Heisig, G. B.: J. Am. Chem. Soc. **73,** 5630 (1951).
(91) Fernando, Q., Emery, J. F., and Phillips, J. P.: J. Am. Chem. Soc. **75,** 1983 (1953).
(92) Fernando, Q., and Phillips, J. P.: J. Am. Chem. Soc. **74,** 3103 (1952).
(93) Fischer, O., and Chur, M.: J. prakt. Chem. [2] **93,** 376 (1917).
(94) Fischer, O., and Renouf, E.: Ber. **17,** 756 (1884).
(95) Fischer, O., and Renouf, E.: Ber. **17,** 1642 (1884).
(96) Flagg, J. F.: *Organic Reagents*, pp. 157–90. Interscience Publishers, Inc., New York (1948).
(97) Fox, J. J.: J. Chem. Soc. **97,** 1339 (1910).
(98) Frankel, S., and Grauer, O.: Ber. **46,** 2552 (1913).
(99) Frankel, S., and Lowy, P.: Ber. **46,** 2546 (1913).
(100) Frere, F. J.: J. Am. Chem. Soc. **55,** 4362 (1933).
(101) Fresenius, P.: Arzneimittel-Forsch. **1,** 180 (1951); Chem. Abstracts **45,** 10502 (1951).
(102) Fritzche and Co.: German patent 187,869; Frdl. **8,** 1200.
(103) Fujise, S.: Sci. Papers, Inst. Phys. Chem. Research **8,** 161 (1928); Chem. Abstracts **22,** 3890 (1928).
(104) Gabbard, R. B., and Foye, W. O.: Abstracts of Papers Presented before the Division of Organic Chemistry at the 126th Meeting of the American Chemical Society, New York City, September 12–17, 1954, p. 45-O.
(105) Gabel, Y. O., and Zubarovskiĭ, V. M.: Khim. Referat. Zhur. **2,** No. 4, **55** (1939); Chem. Abstracts **34,** 1015 (1940).
(106) Garner, C. S.: Brookhaven Conference Report BNL-C-8, Isotopic Exchange Reactions and Chemical Kinetics, Chemical Conference No. 2, p. 94 (1948).
(107) Gengrinovich, A. I.: Farmatsiya **9,** No. 6, 5 (1946); Chem. Abstracts **41,** 7662 (1947).
(108) Ghosh, T. N., Laskar, S. L., and Banerjee, S.: J. Indian Chem. Soc. **21,** 352 (1944); Chem. Abstracts **39,** 2998 (1945).
(109) Ghosh, T. N., Roy, A. C., and Banerjee, S.: J. Indian Chem. Soc. **22,** 219 (1945).
(110) Gilman, H., Towle, J. L., and Spatz, S. M.: J. Am. Chem. Soc. **68,** 2017 (1946).
(111) Gleu, K., and Jagemann, W.: J. prakt. Chem. [2] **145,** 262 (1936).
(112) Grier, N., and Casalbore, C.: U. S. patent 2,489,530 (1949); Chem. Abstracts **44,** 4044 (1950).
(113) Gutzeit, G.: Helv. Chim. Acta **12,** 719 (1929).
(114) Gutzeit, G., and Monnier, R.: Helv. Chim. Acta **16,** 223 (1933).
(115) Gutzeit, G., and Monnier, R.: Helv. Chim. Acta **16,** 239 (1933).
(116) Gutzeit, G., and Monnier, R.: Helv. Chim. Acta **16,** 478 (1933).
(117) Haase, L. W.: Z. anal. Chem. **78,** 116 (1929).
(118) Hackl, O.: Z. anal. Chem. **109,** 91 (1937).
(119) Hall, N. F., and Willeford, B. R.: J. Am. Chem. Soc. **73,** 5419 (1951).
(120) Hanhart, W.: U. S. patent 2,671,775 (1954); Chem. Abstracts **48,** 9701 (1954).
(121) Harvey, B. G., Heal, H. G., Maddock, A. G., and Rowley, E. L.: J. Chem. Soc. **1947,** 1010.
(122) Haworth, R. D., Lamberton, A. H., and Woodcock, D.: J. Chem. Soc. **1947,** 182.
(123) Hebebrand, A.: Ber. **21,** 2979 (1888).
(124) Hein, F., and Regler, H.: Ber. **69B,** 1692 (1936); **74B,** 1926 (1941).
(125) Helin, A. F., and VanderWerf, C. A.: J. Org. Chem. **17,** 229 (1952).
(126) Hollingshead, R. G. W.: Chemistry & Industry **1954,** 344, No. 12.
(127) Hoo, V., Ma, T. S., and Sah, P. P. T.: Science Repts. Natl. Tsinghua Univ. **2,** 191 (1933); Chem. Abstracts **28,** 3692 (1934).
(128) Hume, D. N., and Stone, H. W.: J. Am. Chem. Soc. **63,** 1200 (1941).
(128a) I. G. Farbenindustrie A.-G.: See references 84–85.
(129) Irving, H., Butler, E. J., and Ring, M.: J. Chem. Soc. **1949,** 1489.
(130) Irving, H., and Rossotti, H. S.: J. Chem. Soc. **1954,** 2910.
(131) Irving, H., and Williams, R. J. P.: J. Chem. Soc. **1953,** 3207.

(132) Isiwara, K.: Japanese patent 94,165 (1932); Chem. Abstracts **27,** 2697 (1933).
(133) Johnston, W. D., and Freiser, H.: J. Am. Chem. Soc. **74,** 5239 (1952).
(134) Kanevskaya, S. I., and Melent'eva, G. A.: Sbornik. Stateĭ Obshcheĭ Khim., Akad. Nauk S.S.S.R. **1,** 679 (1953); Chem. Abstracts **49,** 1041 (1955).
(135) Kaufmann, A., and Rothlin, E.: Ber. **49,** 581 (1916).
(136) Kaufmann, H. P., and Huang, L. S.: Ber. **75,** 1217 (1942).
(137) Kaufmann, P., and Weber, E.: Arch. Pharm. **267,** 192 (1929).
(138) King, W. R., and Garner, C. S.: J. Chem. Phys. **18,** 689 (1950).
(139) Kogan, M., and Raikhman, K. M.: J. Applied Chem. (U.S.S.R.) **12,** 1393 (1939); Chem. Abstracts **34,** 3274 (1940).
(140) Kostanecki, S. von: Ber. **24,** 152 (1891).
(141) Kostanecki, S. von, and Reicher, M.: Ber. **24,** 156 (1891).
(142) Kruh, R., and Diggins, C. W.: J. Am. Chem. Soc. **77,** 806 (1955).
(143) Kudo, I., and Nakatsuka, Y.: J. Inst. Polytech. Osaka City Univ., Ser. C, **4,** 50 (1953); Chem. Abstracts **48,** 3177 (1954).
(144) Kuhn, R., and Westphal, O.: Ber. **73B,** 1105 (1940).
(145) Kul'berg, L. M., Mustafin, I. S., and Cherkesov, A. I.: Ukrain. Khim. Zhur. **18,** 547 (1952); Chem. Abstracts **48,** 5016 (1954).
(146) Kuroya, H., Aimi, M., and Tsuchida, R.: J. Chem. Soc. Japan **64,** 975 (1943); Chem. Abstracts **41,** 4731 (1947).
(147) Kuznetsov, V. I.: Zhur. Obshcheĭ Khim. **20,** 807 (1950); Chem. Abstracts **45,** 1452 (1951).
(148) Lacroix, S.: Anal. Chim. Acta **1,** 260 (1947).
(149) Lapkina, N. B.: J. Gen. Chem. (U.S.S.R.) **16,** 1737 (1946); Chem. Abstracts **41,** 5883 (1947).
(150) Laskar, S. L.: J. Indian Chem. Soc. **23,** 231 (1946); Chem. Abstracts **41,** 2055f (1947).
(151) Laskowski, D. E., Grabar, D. G., and McCrone, W. C.: Anal. Chem. **25,** 1400 (1953).
(152) Lavollay, J.: *Applications de la 8-hydroxyquinoleine à l'analyse biologique et agricole.* Hermann et Cie., Paris (1937).
(153) Leffler, M. T., and Matson, E. J.: J. Am. Chem. Soc. **70,** 3439 (1948).
(154) Lindenstruth, A. F., and VanderWerf, C. A.: J. Am. Chem. Soc. **71,** 3020 (1949).
(155) Linnell, W. H., and Vora, S. V.: J. Pharm. and Pharmacol. **3,** 670 (1951); Chem. Abstracts **46,** 2060 (1952).
(156) Lippmann, E.: Monatsh. **8,** 439 (1887).
(157) Lippmann, E., and Fleissner, F.: Ber. **19,** 2468 (1886).
(158) Lippmann, E., and Fleissner, F.: Monatsh. **9,** 297 (1888).
(159) Lippmann, E., and Fleissner, F.: Monatsh. **10,** 665 (1889).
(160) Lippmann, E., and Fleissner, F.: Monatsh. **10,** 794 (1888).
(161) Long, R., and Schofield, K.: J. Chem. Soc. **1953,** 3161.
(162) Luis, A., and Palomo, G.: Afinidad **28,** 163 (1951); Chem. Abstracts **47,** 10533 (1953).
(163) Mackie, A., and Cutler, A. A.: Rec. trav. chim. **71,** 1198 (1952).
(164) Magidson, O. Y., and Rubtzov, M. V.: Khim. Farm. Prom. **1935,** No. 1, 20; Chem. Abstracts **30,** 1789 (1936).
(165) Maksimova, N. V., and Kozlovskiĭ, M. T.: Zhur. Anal. Khim. **2,** 353 (1947); Chem. Abstracts **43,** 7374 (1949).
(166) Maley, L. E., and Mellor, D. P.: Australian J. Sci. Research **2A,** 92 (1949).
(167) Manasse, O.: Ber. **27,** 2412 (1894).
(168) Manasse, O.: Ber. **35,** 3844 (1902).
(169) Mander-Jones, B., and Trikojus, V. M.: J. Proc. Roy. Soc. N.S. Wales **66,** 300 (1932); Chem. Abstracts **27,** 1350 (1933).
(170) Manske, R. F. H., Ledingham, A. E., and Ashford, W. R.: Can. J. Research **27F,** 359 (1949).
(171) Marchilhacy, D. M. G., and Horclois, R. J.: U. S. patent 2,499,661 (1950); Chem. Abstracts **44,** 5399 (1950).
(172) Matheus, J.: Ber. **21,** 1644 (1888).

(173) Matsumura, K.: J. Am. Chem. Soc. **49,** 813 (1927).
(174) Matsumura, K.: J. Am. Chem. Soc. **52,** 4164 (1930).
(175) Matsumura, K.: J. Am. Chem. Soc. **52,** 4433 (1930).
(176) Matsumura, K.: J. Am. Chem. Soc. **57,** 124 (1935).
(177) Matsumura, K., and Sone, C.: J. Am. Chem. Soc. **53,** 1493 (1931).
(178) McAllister, R. A.: Analyst **79,** 522 (1954).
(179) Mellor, D. P., and Maley, L. E.: Nature **159,** 370 (1947).
(180) Mel'nikov, N. N., Sklyarenko, S. I., and Cherkasova, E. M.: J. Gen. Chem. (U.S.S.R.) **9,** 1819 (1939); Chem. Abstracts **34,** 3699 (1940).
(181) Merritt, L. L.: Anal. Chem. **25,** 718 (1953).
(182) Merritt, L. L., Cady, R. T., and Mundy, B. W.: Acta Cryst. **7,** 473 (1954).
(183) Mills, J. E., and Mellor, D. P.: J. Am. Chem. Soc. **64,** 181 (1942).
(184) Mitchell, P. D.: J. Gen. Microbiol. **3,** 385 (1949); Chem. Abstracts **44,** 3561 (1950).
(185) Moeller, T., and Cohen, A. J.: Anal. Chem. **22,** 686 (1950).
(186) Moeller, T., and Cohen, A. J.: J. Am. Chem. Soc. **72,** 3546 (1950).
(187) Moeller, T., and Jackson, D. E.: Anal. Chem. **22,** 1393 (1950).
(188) Moeller, T., and Pundsack, F. L.: J. Am. Chem. Soc. **76,** 617 (1954).
(189) Moeller, T., and Ramaniah, M. V.: J. Am. Chem. Soc. **75,** 3946 (1953).
(190) Molland, J.: Arch. Math. Naturvidenskab **43,** 67–184 (1940).
(191) Moness, E., and Christiansen, W. G.: J. Am. Pharm. Assoc. **25,** 501 (1936).
(192) Montequi, R., and Gallego, M.: Anales soc. españ. fís. y quím. (Madrid) **32,** 134 (1934); Chem. Abstracts **28,** 3409 (1934).
(193) Monti, L., and Delitala, M.: Gazz. chim. ital. **72,** 520 (1942).
(194) Mueller, M. B.: U. S. patent 2,436,660 (1948); Chem. Abstracts **42,** 4203 (1948).
(195) Mukherjee, S. L.: Indian patent 34,380 (1948); Chem. Abstracts **43,** 697 (1949).
(196) Nador, K.: Magyar Kém. Folyóirat **56,** 58 (1950); Chem. Abstracts **46,** 7547 (1952).
(197) Näsanen, R.: Acta Chem. Scand. **5,** 1293 (1951).
(198) Näsanen, R.: Acta Chem. Scand. **6,** 352 (1952).
(199) Näsanen, R.: Suomen Kemistilehti **26B,** No. 2, 11 (1953); Chem. Abstracts **47,** 9724 (1953).
(200) Näsanen, R., and Penttinen, U.: Acta Chem. Scand. **6,** 837 (1952).
(201) Nagase, Y.: Bunseki to Shiyaku (Chem. Analysis and Reagent) **2,** 163 (1947); Chem. Abstracts **47,** 3855 (1953).
(202) Nakatsuka, Y.: Bull. Chem. Soc. Japan **11,** 45 (1936); Chem. Abstracts **30,** 4115 (1936).
(203) Nakatsuka, Y., and Chang, T.: Acta Chimica Teiwanica **1,** 37 (1949).
(204) Nakatsuka, Y., and Kudo, I.: J. Inst. Polytech., Osaka City Univ., Ser. C, **1,** 5 (1951); Chem. Abstracts **46,** 4924 (1952).
(205) Nakatsuka, Y., and Kudo, I.: J. Chem. Soc. Japan, Pure Chem. Sect. **72,** 655 (1951); Chem. Abstracts **46,** 6981 (1952).
(206) Nakatsuka, Y., and Miwa, T.: J. Inst. Polytech., Osaka City Univ., Ser. C, **3,** 37 (1952); Chem. Abstracts **47,** 9846 (1953).
(207) Neu, R.: Z. anal. Chem. **142,** 335 (1952).
(208) Niementowski, S. von, and Sucharda, E.: Ber. **49,** 13 (1916).
(209) Noelting, E.: Chimie & industrie **8,** 758 (1922).
(210) Nogradi, T.: Chem. Ber. **85,** 104 (1952).
(211) Oettingen, W. F. van: *Therapeutic Agents of the Quinoline Group,* p. 33 ff. Chemical Catalog Company, New York (1933).
(212) Ohta, T., and Okuda, O.: J. Pharm. Soc. Japan **71,** 784 (1951).
(213) Panouse, J. J.: Compt. rend. **230,** 846 (1950); Chem. Abstracts **45,** 1589 (1951).
(214) Panthaleon Van Eck, C. L.: Rec. trav. chim. **72,** 50 (1953).
(215) Papesch, V., and Burtner, R. R.: J. Am. Chem. Soc. **58,** 1314 (1936).
(216) Passek, F.: German patent 411,050 (1925); Chem. Zentr. **1925, I,** 2412.

(217) Patton, R. L.: National Nuclear Energy Series, Div. IV, 14B, Transuranium Elements, Pt. I, p. 853 (1949).
(218) Petrow, V., and Sturgeon, B.: J. Chem. Soc. **1954,** 570.
(219) Phillips, J. P.: Unpublished results.
(220) Phillips, J. P., Elbinger, R. L., and Merritt, L. L.: J. Am. Chem. Soc. **71,** 3984 (1949).
(221) Phillips, J. P., Emery, J. F., and Fernando, Q.: J. Am. Chem. Soc. **74,** 5542 (1952).
(222) Phillips, J. P., and Fernando, Q.: J. Am. Chem. Soc. **75,** 3768 (1953).
(223) Phillips, J. P., and Keown, R.: J. Am. Chem. Soc. **73,** 5483 (1951).
(224) Phillips, J. P., Keown, R., and Fernando, Q.: J. Am. Chem. Soc. **75,** 4306 (1953).
(225) Phillips, J. P., Keown, R., and Fernando, Q.: J. Org. Chem. **19,** 907 (1954).
(226) Phillips, J. P., and O'Hara, F. J.: Anal. Chem. **23,** 535 (1951).
(227) Phillips, J. P., and Price, H. P.: J. Am. Chem. Soc. **73,** 4414 (1951).
(228) Pirrone, F.: Gazz. chim. ital. **66,** 518 (1936); Chem. Abstracts **31,** 3921 (1937).
(229) Pirrone, F.: Gazz. chim. ital. **67,** 529 (1937); Chem. Abstracts **32,** 1701 (1938).
(230) Pirrone, F.: Atti accad. Italia, Rend. classe sci. fis., mat. nat. [7] **1,** 50 (1939); Chem. Abstracts **34,** 5450 (1940).
(231) Pirrone, F.: Gazz. chim. ital. **70,** 520 (1940); **71,** 320 (1941).
(232) Pirrone, F., and Cherubino, A.: Atti accad. Lincei **18,** 311 (1933); Chem. Abstracts **28,** 3073 (1934).
(233) Pirrone, F., and Cherubino, A.: Gazz. chim. ital. **65,** 743 (1935); Chem. Abstracts **30,** 2194 (1936).
(234) Pirtea, T.: Bul. Chim., Soc. Române Chim. **39,** 83 (1937); Chem. Abstracts **34,** 2277 (1940).
(235) Pirtea, T.: Z. anal. Chem. **118,** 26 (1939).
(236) Pokras, L., and Bernays, M.: J. Am. Chem. Soc. **73,** 7 (1951).
(237) Pokras, L., and Bernays, M.: Anal. Chem. **23,** 757 (1951).
(238) Pokras, L., Kilpatrick, M., and Bernays, M.: J. Am. Chem. Soc. **75,** 1254 (1953).
(239) Pratt, Y. T., and Drake, N. L.: J. Am. Chem. Soc. **77,** 4664 (1955).
(240) Prodinger, W., and Svoboda, O.: Monatsh. **85,** 23 (1954).
(241) Ramsey, W. J., Douglas, D. L., and Yost, D. M.: J. Am. Chem. Soc. **72,** 2782 (1950).
(242) Ray, S. K., and Sen, R. N.: J. Indian Chem. Soc. **25,** 473 (1948).
(243) Reichel, L., and Ilberg, K.: Ber. **76B,** 1108 (1943).
(244) Rey, A. B.: Ion **7,** 389 (1947).
(245) Ringier, B. H.: Helv. Chim. Acta **27,** 1790 (1944).
(246) Rosenmund, K. W., and Doring, H.: Arch. Pharm. **266,** 277 (1928).
(247) Rosenmund, K. W., and Karst, G.: Arch. Pharm. **279,** 154 (1941).
(248) Ruben, S., Kamen, M. D., Allen, M. B., and Nahinsky, P.: J. Am. Chem. Soc. **64,** 2297 (1942).
(249) Sah, P. P. T.: Rec. trav. chim. **69,** 1407 (1950).
(250) Sanchez, J. V., and Romo, A. H.: Bol. inst. quím. univ. nacl. auton. Méx. **2,** No. 2, 77 (1946); Chem. Abstracts **43,** 7484 (1949).
(251) Sandell, E. B., and Spindler, D. C.: J. Am. Chem. Soc. **71,** 3806 (1949).
(252) Schafer, H., and Braun, O.: Naturwissenschaften **39,** 280 (1952); Chem. Abstracts **47,** 6299 (1953).
(253) Schenkel-Rudin, H. and M.: Helv. Chim. Acta **27,** 1456 (1944).
(254) Schmitt, R., and Engelmann, F.: Ber. **20,** 1217, 2690 (1887).
(255) Schneiderwirth, H. J.: U. S. patent 2,121,449 (1938); Chem. Abstracts **32,** 6262 (1938).
(256) Schüller, H.: J. prakt. Chem. [2] **88,** 180 (1913).
(257) Seguin, M.: Compt. rend. **222,** 952 (1946).
(258) Seguin, M.: Bull. soc. chim. **1946,** 566.
(259) Sen, R. N., and Mukherjee, G. K.: J. Indian Chem. Soc. **11,** 541 (1934); Chem. Abstracts **28,** 7258 (1934).

(260) Sen, R. N., and Ray, S. K.: J. Indian Chem. Soc. **9,** 178 (1932).

(261) Sen-Gupta, R.: J. Indian Chem. Soc. **22,** 171 (1945).

(262) Shchunkina, M. N., and Savitskaya, N. V.: Zhur. Obshcheĭ Khim. **22,** 1218 (1952); Chem. Abstracts **47,** 7505 (1953).

(263) Shchunkina, M. N., and Savitskaya, N. V.: Zhur. Obshcheĭ Khim. **22,** 1224 (1952); Chem. Abstracts **47,** 7506 (1953); **48,** 2709 (1954).

(264) Shreve, R. N., and Bennett, R. B.: J. Am. Chem. Soc. **65,** 2243 (1943).

(265) Silverman, L., Moudy, L., and Hawley, D. W.: Anal. Chem. **25,** 1369 (1953).

(266) Skraup, H.: Monatsh. **3,** 536 (1882).

(267) Skrowaczewska, Z.: Roczniki Chem. **22,** 154 (1948); Chem. Abstracts **44,** 3494 (1950).

(268) Société anon. pour l'industrie chimique a Bale: German patent 556,324 (1930); Chem. Abstracts **26,** 5573 (1932).

(269) Société pour l'industrie chimique à Bâle: Swiss patent 208,000 (1940); Chem. Abstracts **35,** 3649 (1941).

(270) Société pour l'industrie chimique à Bâle: British patent 536,367 (1941); Chem. Abstracts **36,** 1617 (1942).

(271) Société belge de l'azote et des produits chimiques du Marly S. A.: Belgian patent 499,762 (1951); Chem. Abstracts **48,** 4186 (1954).

(272) Société des usines chimiques Rhône-Poulenc: British patent 626,007 (1949); Chem. Abstracts **44,** 4045 (1950).

(273) Sone, K.: J. Am. Chem. Soc. **75,** 5207 (1953).

(274) Sowa, F. J., and Kenney, E. J.: U. S. patent 2,580,473 (1952); Chem. Abstracts **46,** 4823 (1952).

(275) Spacu, G., and Macarovici, C. G.: Bull. sect. sci. acad. roumaine **22,** 150 (1939); Chem. Abstracts **34,** 3200 (1940).

(276) Steiger, N.: Dissertation, Wurzburg, 1915, p. 41.

(277) Stock, J. T.: J. Chem. Soc. **1949,** 586.

(278) Sucharda, E.: Ber. **58,** 1728 (1925).

(279) Sudborough, J. J., and Beard, S. H.: J. Chem. Soc. **99,** 213 (1911).

(280) Sue, P., and Wetroff, G.: Bull. soc. chim. [5] **2,** 1002 (1935).

(281) Sullivan, M. V., and Hunt, H.: J. Phys. Chem. **53,** 497 (1949).

(282) Sumpter, W. C.: Chem. Revs. **34,** 419 (1944).

(283) Szmaragd, S., and Briner, E.: Helv. Chim. Acta **32,** 1278 (1949).

(284) Taylor, E. P.: J. Chem. Soc. **1952,** 1311.

(285) Thilo, E., and Demant, B.: Ber. **72,** 1048 (1939).

(286) Tinovskaya, E. S.: Zhur. Anal. Khim. **5,** 345 (1950); Chem. Abstracts **45,** 930 (1951).

(287) Towle, J. L.: Iowa State Coll. J. Sci. **26,** 308 (1952).

(288) Usgaonkar, R. N., Chakravarti, K. K., and Thakor, V. M.: J. Sci. Ind. Research (India) **11B,** 396 (1952); Chem. Abstracts **47,** 11195 (1953).

(289) Venkateswarlu, K. S., and Raghava Rao, B. S. V.: Anal. Chim. Acta **12,** 554 (1955).

(290) Vogt, H.: Arch. Pharm. **282,** 27 (1944); Chem. Abstracts **40,** 6759 (1946).

(291) Vorozhtzov, N. N., and Mitzengendler, S. P.: J. Gen. Chem. (U.S.S.R.) **6,** 63 (1936); Chem. Abstracts **30,** 4862 (1936).

(292) Wagner, E. C., and Simons, J. K.: J. Chem. Education **13,** 265 (1936).

(293) Welcher, F. J.: *Organic Analytical Reagents*, Vol. I, pp. 263–356. D. Van Nostrand Co., Inc., New York (1947).

(294) Wheatley, W. B.: U. S. patent 2,649,451 (1953); Chem. Abstracts **48,** 9409 (1954).

(295) Wheatley, W. B., Cheney, L. C., and Brinkley, S. B.: J. Am. Chem. Soc. **71,** 3795 (1949).

(296) White, C. E., Fletcher, M. H., and Parks, J.: Anal. Chem. **23,** 478 (1951).

(297) Widmer, W.: U. S. patent 2,475, 265 (1949); Chem. Abstracts **44,** 6651 (1950).

(298) Wiederkehr, F. X., and Hofstetter, E.: Helv. Chim. Acta **35,** 468 (1952).

(299) Willis, J. B., amd Mellor, D. P.; J. Am. Chem. Soc. **69,** 1237 (1947).

(300) WILLSTAEDT, H., AND BORGGARD, M.: Svensk Kem. Tid. **57,** 254 (1945); Chem. Abstracts **40,** 5437 (1946).
(301) WOLFFENSTEIN: German patent 281,007; Frdl. **12,** 729.
(302) WOROSHTZOW, N. N., AND KOGAN, J. M.: Ber. **63,** 2356 (1930).
(303) WOROSHTZOW, N. N., AND KOGAN, J. M.: Ber. **65,** 142 (1932).
(304) WURTZ, C. A.: Compt. rend. **96,** 1269 (1883).
(305) ZEIFMAN, V.: Khim. Referat. Zhur. **1939,** No. 6, 46.
(306) ZETSCHE, F., SILBERMAN, H., AND VIELI, G.: Helv. Chim. Acta **8,** 602 (1925).
(307) ZHEDEK, M. S.: Zhur. Priklad. Khim. **25,** 109 (1952); Chem. Abstracts **47,** 867 (1953).
(308) ZHEDEK, M. S.: J. Applied Chem. (U.S.S.R.) **25,** 115 (1952); Chem. Abstracts **47,** 2990 (1953).