AD

CCL REPORT NO. 207

PROGRESS REPORT

DERIVATIVES OF 8-QUINOLINOL

BY

MARJAN KOLOBIELSKI

AUGUST 1966

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

U. S. ARMY COATING & CHEMICAL LABORATORY
Aberdeen Proving Ground
Maryland

UNCLASSIFIED

CCL REPORT NO. 207

PROGRESS REPORT

DERIVATIVES OF 8-QUINOLINOL

BY

MARJAN KOLOBIELSKI

AUGUST 1966

AMCMS CODE NO. 5016.11.844

DEPARTMENT OF THE ARMY PROJECT NO.
1L013001A039

U.S. ARMY COATING AND CHEMICAL LABORATORY
ABERDEEN PROVING GROUND
MARYLAND

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

UNCLASSIFIED

ABSTRACT

The overall objective of this project is the establishment of the relation of the hydrophilic-lipophilic ratios of chelating compounds and selected solvents to the corrosion inhibitory action of these compounds in various solvents. Derivatives of 8-quinolinol containing different substituents were selected as the chelates for the initial investigation of physical properties such as dissociation constants, stability constants, hydrophilic-lipophilic ratios and of their corrosion inhibitory action. The results obtained may also allow one to relate the effect on corrosion inhibition of the molecular structure of these derivatives. In this study the needed derivatives were prepared in high purity and their structure proved by the use of non-equivocal synthetic means. The majority of the compounds are new products derived from 8-quinolinol and containing groups such as alkyl, hydroxy, alkoxy, amine and polyethylenoxy. The new compounds besides being considered as corrosion inhibitors may in some cases be potential additives for liquid fuels as antioxidants and metal deactivators, and will be screened for such possibilities.

TABLE OF CONTENTS

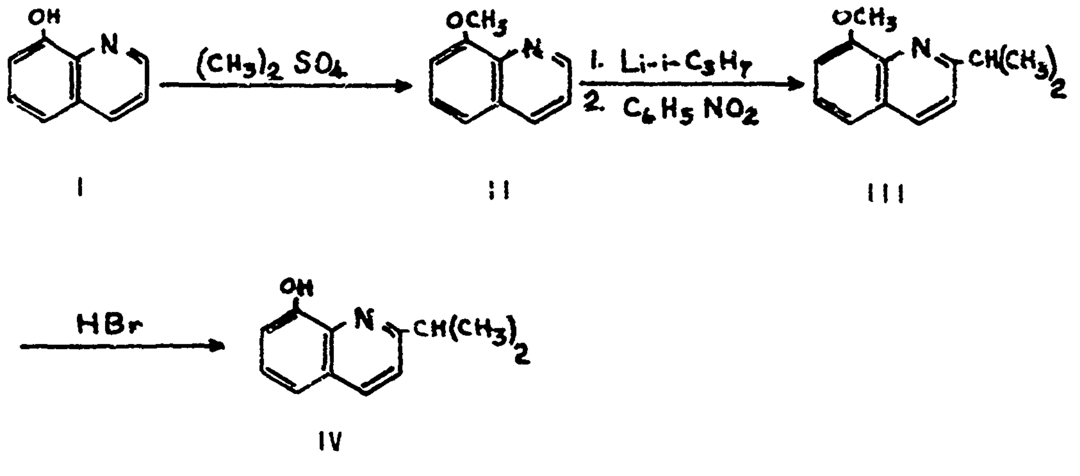
I. INTRODUCTION

This work is a part of a project whose broad scientific objective is to establish if corrosion inhibitory action of chelates is a function of the hydrophilic-lipophilic ratios of the chelating compounds as well as that of the solvent used. Since 8-quinolinol or "Oxine" itself is a known chelating agent (1), (2) it was selected as a starting material for this study. It was expected that derivatives of 8-quinolinol containing functional groups alkyl or alkoxy, hydroxy, amine and polyethylenoxy at different positions of the molecule would have various hydrophilic-lipophilic ratios. These derivatives may have dissociation constants different from those of 8-quinolinol and give metal chelates possessing different stability constants. Furthermore one may expect that the substituted hydroxy quinolines would have different corrosion inhibitory properties. In this report is described the synthesis of the derivatives having alkyl substituents at positions 2 and 7 and derivatives possessing hydroxy, alkoxy, amine, and polyethylenoxy groups at position 5.

II. DETAILS OF THE STUDY

A. Methods of Preparation - General

The compounds prepared in this work are derivatives of 8-quinolinol having substituents in position 2 or 5 or 7. The new 2-isopropyl-8-quinolinol (IV) was prepared by several step synthesis involving methylation of commercial 8-quinolinol (I) with dimethyl sulfate (3) to 8-methoxyquinoline (II), alkylation of II with isopropyl lithium at low temperature, following the procedure applied to quinoline (4) and 8-quinolinol (5), and finally demethylation of the intermediate 2-isopropyl-8-methoxyquinoline (III).



The final product IV was a crystalline solid in contrast to the known n-propyl isomer (5), 2-propyl-8-quinolinol which is a liquid. The 7-isopropyl-8-quinolinol (IX a) was prepared by a three-step synthesis from 2-isopropyl phenol (V a). Nitration of V a at -15 to -12°C using 2 mole-equivalents of nitric acid per mole-equivalent of 2-isopropylphenol gave a mixture of two compounds: a yellow liquid 2-isopropyl-6-nitrophenol (VI a), and a yellow solid (mp 54-55°C) 2-isopropyl-4, 6-dinitrophenol (VII a). The two nitroderivatives were separated and the structures of the pure compounds proved by elemental, infrared and nmr spectroscopic analyses.

In both compounds the presence of a nitro group in ortho position to the phenolic hydroxyl was confirmed by the infrared spectra. The spectra of solutions of VIa and VIIa in carbon tetrachloride show a hydroxyl group frequency at 3175 and 3125 cm^{-1} respectively, much lower than that of phenol, because in both compounds there is a hydrogen bonding (6) of the OH to the ortho nitro group.

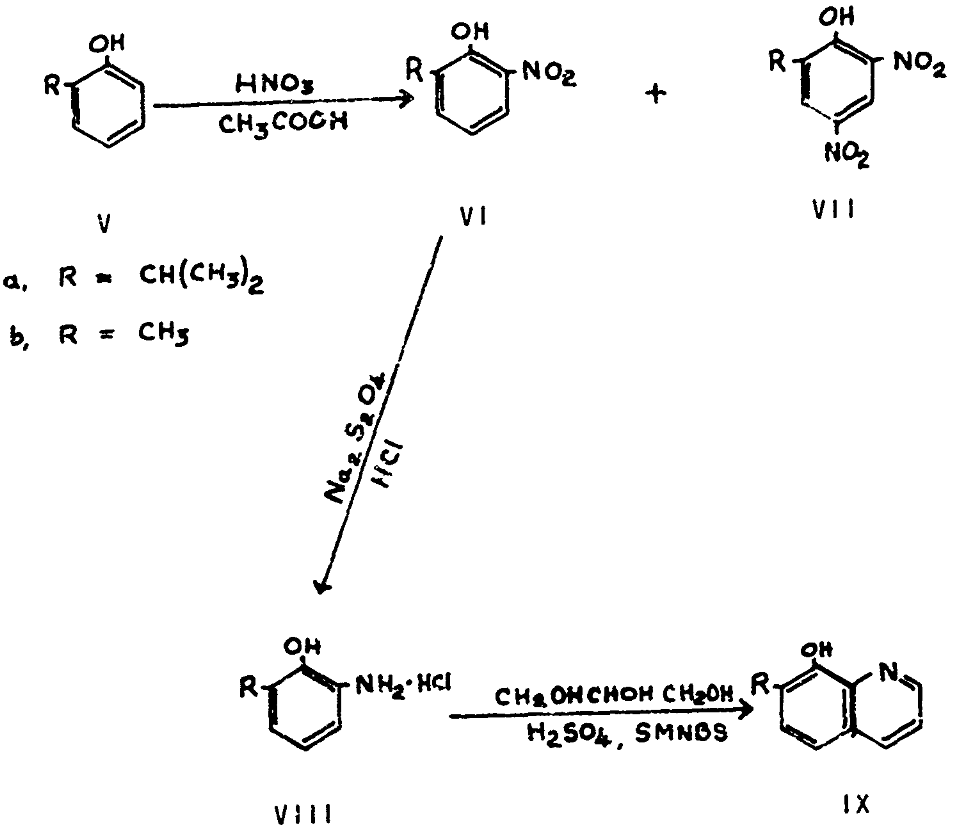
The nmr spectrum of VIa indicates the presence of three benzene ring protons in positions 3, 4, and 5 while that of VII a two benzene ring protons in positions 3 and 5 in agreement with their structures. According to Fileti (7) nitration under different conditions gives a mixture of two nitro isomers, a liquid presumably impure 2-isopropyl-6-nitrophenol, having an imperfect elemental analysis and another a colorless solid, 2-isopropyl-4-nitrophenol melting at 86°C. The author (7) did not prove the structure of these isomers.

Reduction of VIa produced the 2-isopropyl-6-aminophenol which, because of its susceptibility to oxidation, was not isolated but converted to its hydrochloride Salt VIIIa. The hydrochloride salt VIIIa gave by the Skraup reaction (8), the crystalline quinolinol IXa. The known n-propyl isomer, 7-propyl-9-quinolinol is reported to be a liquid (9).

The 7-methyl-8-quinolinol (IX b) was prepared by a similar method starting from o-cresol (Vb). Nitration of o-cresol, following the procedure of Gibson (10), gave a mixture of 2-methyl-6-nitrophenol (VI b) and 2-methyl-4-nitrophenol from which the more volatile isomer VIb could be separated in a pure form.

Reduction of VIb gave the 2-methyl-6-amino phenol which as hydrochloride salt VIII b was condensed with glycerine by a Skraup reaction to afford the known 7-methyl-8-quinolinol (IX b) (11).

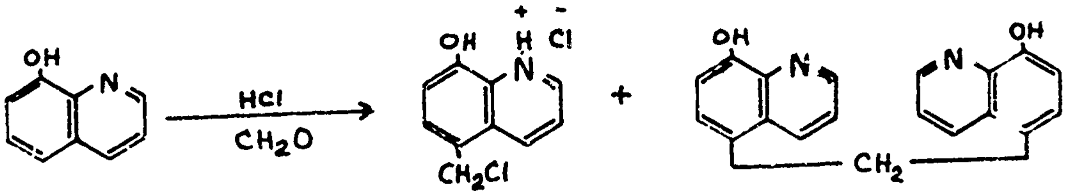
The physical properties of the alkyl-8-quinolinols are summarized in Table I.



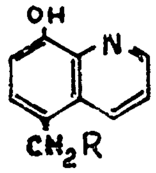
SMNBS: sodium m-nitrobenzenesulfonate

The 5-substituted derivatives of 8-quinolinol were synthesized from 5-chloromethyl-8-quinolinol hydrochloride (X) whose structure was recently established (12), (13). The starting X, prepared by chloromethylation of 8-quinolinol (12), (13, (14), is difficult to purify (13) because of its great reactivity. Usually it contains small amounts of unreacted 8-quinolinol (1) and 5, 5' - methylene bis-8-quinolinol (XI) (12). The bisphenol XI was prepared directly by reacting I with formaldehyde in a molar ratio of two to one respectively in the presence of sulfuric acid (12), (13), (15). The chloromethyl compound X is readily hydrolized to 5-hydroxymethyl-8-quinolinol (XII) (12) and therefore the alcohol XII is often found as a by-product in the reaction mixture obtained upon treatment of X with reagent containing traces of water. It was found in this study that prolonged chloromethylation of 8-quinolinol at room temperature followed by slow crystallization affords crystals of higher purity and in good yield.

The treatment of X with alcohols gave the ethers XIII-XVII, new compounds except XIV (13). Condensation of X with secondary amines afforded the tertiary amines XVIII - XXI in high yield, However from the reaction of X with n-propylamine only the tertiary amine XXVII could be isolated in pure form although an excess of the propylamine was used. The amine XIX was reported previously (13). The ether-alcohols XXII and XXIII and polyethers XXIV - XXVI were obtained by reacting X with ethylene glycol, diethylene glycol and the appropriate derivatives of the glycols. A 14-20 molar excess of the glycols was used to obtain the monosubstituted products XXII and XXIII. No base was necessary to effect the above displacement reactions. The physical properties of 5-substituted - 8 - quinolinols are summarized in Table II.



I X XI



XII, R = OH

XIII, R = OCH_3

XIV, R = $OCH(CH_3)_2$

XV, R = OC_5H_{11}

XVI, R = OC_6H_{13}

XVII, R = OC_7H_{15}

XVIII, R = $N(CH_3)_2$

XIX, R = $N(C_2H_5)_2$

XX, R = $N(C_3H_7)_2$

XXI, R = $N(C_4H_9)_2$

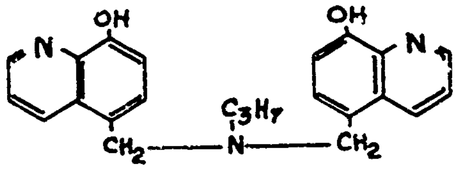
XXII, R = OCH_2CH_2OH

XXIII, R = $O(CH_2CH_2O)_2H$

XXIV, R = $OCH_2CH_2OCH_3$

XXV, R = $O(CH_2CH_2O)_2CH_3$

XXVI, R = $O(CH_2CH_2O)_3CH_3$



XXVII

B. Preparation of Compounds - Details.

8-Methoxyquinoline (II)

A 500 ml. solution of 0.8 N sodium hydroxide was heated and stirred at 70°C. together with 58 g. (0.4 mole) of 8-quinolinol until a homogeneous solution was obtained. The solution was cooled to 25° and methyl sulfate (51 g., 0.4 mole) was introduced over a period of 30 minutes. After addition of sodium hydroxide (10 g.) the reaction mixture was heated on a steam bath for 5 minutes. After cooling it was extracted with ether, and the ether layer washed with water and then dried. Vacuum distillation gave 8-methoxyquinoline bp 113-123°/0.3 mm., 27 g. (42%), mp 41-43°. After recrystallization from hexane-benzene the product melted at 44-45°. [Lit. (3) m.p. 46-47°]

2-Isopropyl-8-quinolinol (IV)

Sixty ml. (0.13 mole) of 2.16 molar solution of isopropyllithium was cooled to -20° under helium atmosphere. A solution of 15.9 g. (0.1 mole) of 8-methoxyquinoline in 200 ml. of ether was introduced over a period of 45 minutes while the temperature was maintained at -25 to -35° by cooling in a dry ice - acetone bath. The reaction mixture was allowed to come to 0° and then poured onto ice. Ether extraction gave, after removal of the solvent, a yellow oil composed of 2-isopropyl-8 methoxy - 1, 2 - dihydroquinoline. The oil was oxidized by heating it at reflux with 70 ml. of nitrobenzene over a period of 20 minutes. After cooling, the solution was diluted with ether and then washed with 2 N hydrochloric acid. The combined aqueous washings were made alkaline with sodium hydroxide and the precipitated oil extracted with ether. The ether was removed by distillation and the oily residue (9.4 g.) composed of 2-isopropyl-8-methoxyquinoline was hydrolized by heating it at reflux with 40 g. of 49% hydrobromic acid over a period of 12 hours. The excess of hydrobromic acid was removed by vacuum distillation and the residue made alkaline with aqueous solution of sodium bicarbonate. The precipitated brown solid was separated by filtration and purified by steam distillation. The collected distillate (1.5 l.) gave 3.7 g. (20%) of 2-isopropyl-8-quinolinol melting at 84-88°. Recrystallization from pentane raised the melting point to 89 - 91°.
Anal. Calc'd. for $C_{12}H_{13}NO$: C,77.00; H,6.95; N,7.49.
Found: C,76.93; H,6.80; N,7.54.

2-Isopropyl-6-nitrophenol (VIa) and 2-Isopropyl-4, 6-dinitrophenol (VIIa)

To a stirred solution of 90 ml. (1.42 mole) of concentrated (70%, d 1.42) nitric acid in 180 ml. of glacial acetic acid cooled to -15° was introduced dropwise over a period of 2.5 hour a solution of 90 g. (0.66 mole) of freshly distilled o-isopropyl phenol in 90 ml. of glacial acetic acid. During the addition, the temperature was maintained at -15 to -12°. An additional 90 ml. of glacial acetic acid was added and the mixture stirred for an additional hour. The reaction mixture was then poured into 4 l. of water, and steam distilled. The distillate gave two main fractions, the first containing 5 l. and another containing 50 l. The first fraction after ether extraction and removal of the solvent gave a liquid residue. The second fraction containing a yellow solid afforded by filtration 68.4 g. of a product melting at 53 - 55°. The liquid residue, from the first fraction, contained as impurities acetic and nitric acids. The acids were removed by distillation at 70 - 80° (bath temp.) and 0.1 mm. The liquid residue was dissolved in ether and the ethereal solution washed with aqueous solution of sodium bicarbonate. The alkaline washings gave upon acidification an additional 6.2 g. of the yellow solid VII a, mp. 53 - 55°. Because the compound VIIa is a dinitrophenol, it is more acidic than VIa and therefore formed a water soluble sodium salt when treated with sodium bicarbonate. The ethereal solution was concentrated and the residue purified by distillation to afford 21 g. (18%) of 2-isopropyl-6-nitrophenol, yellow liquid, bp 131 - 135°/20 mm., n_D^{22} 1.5550.
Anal. Calc'd. for $C_9H_{11}NO_3$: C,59.67; H,6.08; N,7.73;
Found: C,59.62; H,5.94; N,7.75. The total of the combined yellow solid amounted to 74.6 g. (50%). Recrystallization from hexane gave pure 2-isopropyl-4,6-dinitrophenol, melting at 54 - 55°.
Anal. Calc'd. for $C_9H_{10}N_2O_5$: C,47.79; H,4.42; N,12.39.
Found: C,47.80; H,4.38; N, 12.34.
Gas-liquid chromatographic analysis confirmed the high purity of both nitro-compounds.

2-Isopropyl-6-aminophenol hydrochloride (VIIIa)

To a stirred solution of 9.05 g. (0.05 mole) of 2-isopropyl-6-nitrophenol in 240 ml. of 0.25 N sodium hydroxide was introduced sodium hydrosulfite (39 g., 0.225 mole) over a period of 15 mm. The mixture was stirred for 30 min. and then heated at reflux for 5 min. After cooling, it was extracted with ether and the ether layer dried over anh. sodium sulfate. Hydrogen chloride gas was passed through the ethereal solution. The precipitated solid was filtered and washed with ether to give 5.6 g. (60%) of the hydrochloride salt VIIIa, mp 228 - 230° with decomposition. The product darkens on standing.

7-Isopropyl-8-quinolinol (IX a)

A mixture of 10 g. (0.0525 mole) of 2-isopropyl-6-aminophenol hydrochloride, 20 g. (0.22 mole) of glycerol, 22.5 g., (0.1 mole) of sodium m-nitrobenzene sulfonate, and 100 ml. of 65% sulfuric acid was stirred and heated at reflux (~140°) over a period of 4 hours. The mixture was cooled, diluted with water and adjusted to pH 3 with a 15% solution of sodium hydroxide. The precipitated tarry impurity was removed by filtration and the filtrate made alkaline with sodium bicarbonate; dark colored product precipitated. The crude product (7.7 g.) was purified by sublimation at 80-120° (bath temp.) and 0.1 mm. to give 2.6 g. (25%) of crystals which recrystallized from hexane melted at 39-40°.

Anal. Calc'd. for $C_{12}H_{13}NO$: C,77.00; H,6.95; N,7.49.
Found: C,77.14; H,6.99; N,7.47.

2-Methyl-6-nitrophenol (VI b) and 2-methyl-4-nitrophenol

To a stirred solution of 107 ml. (1.7 mole) of conc. (70%, d. 1.42) nitric acid in 300 ml. of glacial acetic acid cooled to -10° was introduced dropwise over a period of 4 hours a solution of 100 g. (0.925 mole) of o-cresol in 100 ml. of glacial acetic acid. During the addition the temperature was maintained at -10 to -12°. The reaction mixture was poured into 4 l. of water and steam distilled. The distillation gave 3 fractions: 34 g. (24%) of 2-methyl-6-nitrophenol, mp 68-69°, 5.4 g. of a mixture of VI b and 2-methyl-4-nitrophenol, and 9 g. (6.5%) of 2-methyl-4-nitrophenol, mp 84-86°. The 2-methyl-6-nitrophenol was purified by crystallization from hexane, mp 68-69°. [Lit. (10) m.p. 70°]

2-Methyl-6-aminophenol hydrochloride (VIII b)

To a stirred solution of 15.3 g. (0.1 mole) of 2-methyl-6-nitrophenol in 625 ml. of 0.2 N sodium hydroxide solution was introduced sodium hydrosulfite (95 g. 0.45 mole) over a period of 20 min. After cooling, it was extracted with ether and the ether layer dried over anhydrous sodium sulfate. Hydrogen chloride gas was passed through the ethereal solution. The precipitated 2-methyl-6-aminophenol hydrochloride was filtered and washed with ether to give 15 g. (94%).

7-Methyl-8-quinolinol (IX b)

A mixture of 15 g. (0.094 mole) of 2-methyl-6-aminophenol hydrochloride, 25 g. (0.27 mole) of glycerol, 25 g. (0.11 mole) of sodium m-nitrobenzene sulfonate, and 120 ml. of 65% sulfuric acid was stirred and heated at reflux for 4 hours. After cooling, the reaction mixture was diluted with 1 l. of water, treated with 15% solution of sodium hydroxide until pH 6-7 was attained and then acidified with acetic acid. The mixture was subjected to steam distillation. The collected distillate containing acetic acid was made alkaline with sodium bicarbonate and the precipitated solid filtered to afford 4.5 g. (30%) of 7-methyl-8-quinolinol, mp 66-68°. Crystallization from hexane raised the melting point to 68-69°. [Lit. (11) m.p. 72-79°]

5-Chloromethyl-8-quinolinol hydrochloride (X)

A mixture of 101.5 g. (0.7 mole) of 8-quinolinol, 250 ml. (3 moles) of conc. hydrochloric acid, and 250 ml. (3.3 moles) of 37% formaldehyde was stirred while hydrogen chloride gas was passed into the solution over a period of 6 hours. The mixture was kept overnight at room temperature. The yellow crystals which had formed were filtered, washed with ether and dried in the presence of calcium chloride and potassium hydroxide at 45-50° in vacuo to give 146 g. (91%), mp 281-283° with decomposition. [Lit. (13) m.p. 280°] Anal. Calc'd. for $C_9H_8ClNO.HCl$: molecular weight, 229.9. Found by titration with sodium hydroxide: mol. weight, 224.9.

5, 5'-Methylene bis-8-quinolinol (XI)

A mixture of 11.6 g. (0.08 mole) of 8-hydroxyquinoline and 1.2 g. (0.04 mole) of paraformaldehyde was dissolved in cold (0°) conc. sulfuric acid. After 15 minutes at 0° the reaction mixture was poured into water and then neutralized with sodium carbonate. The solid which precipitated was crystallized from pyridine to give 6.2 g. (51%) of crude product, m.p. 200-275°. Repeated crystallization from pyridine yielded pure product, m.p. 270-273° with decomposition. [Lit. (15) m.p. 283 - 284°]

5-Methoxymethyl-8-quinolinol (XIII)

A mixture of 23 g. (0.1 mole) of 5-chloromethyl-8-quinolinol hydrochloride and 250 ml. of anhydrous methanol was heated at reflux temperature for 2 hours. The mixture was poured into 1200 ml. of water and made alkaline with 10% sodium bicarbonate solution. The product which precipitated was filtered, then dissolved in ether and the ethereal solution washed with water and dried over anhydrous sodium sulfate. After removal of the solvent the remaining solid (15 g., 79%) melted at 78-80°. It was recrystallized from hexane m.p. 79-80°.
Anal. Calc'd. for $C_{11}H_{11}NO_2$: C,69.84; H,5.82; N,5.71.
Found: C,69.78; H,5.31; 5.75.

5-Isopropoxy-8-quinolinol (XIV)

A mixture of 46 g. (0.[illegible] mole) of 5-chloromethyl-8-quinolinol hydrochloride, 180 g. (3 moles) of isopropyl alcohol and 16.8 g. (0.2 mole) of sodium bicarbonate was stirred and heated on a steam bath for one hour. The excess of isopropyl alcohol was removed by distillation and the solid residue dissolved in water. The solution was made alkaline with sodium bicarbonate. The precipitated solid was filtered and dried to give 40 g. (92%) of XIV, m.p. 64-65°. [Lit. (13) m.p. 65-66°]

5-Pentyloxymethyl-8-quinolinol (XV) and 5-hydroxymethyl-8-quinolinol (XII)

A mixture of 46 g. (0.2 mole) of 5-chloromethyl-8 quinolinol hydrochloride and 176 g. (2 moles) of 1- pentanol was stirred at 115° for 5 hours. The reaction mixture was hot filtered and the insoluble solid washed with ether. The solid hydrochloride salt (12.2 g.) was dissolved in water and made alkaline with sodium bicarbonate. The solid which precipitated, was separated by filtration and dried to give 9 g. of 5-hydroxymethyl-8- quinolinol (XII), m.p. 132-134° alone, and on mixing with an authentic sample (13). The filtrate in pentanol afforded, upon addition of ether, a solid hydrochloride salt (43.2 g.) which was redissolved in water and the aqueous solution made alkaline with sodium bicarbonate. The product which precipitated was extracted with ether and the ethereal solution, after being dried and evaporated, gave 30.3 g. of a solid residue. The material was distilled to give two main fractions, bp. 70-75°/ 0.05 mm., 5.2 g. of 8-quinolinol, m.p. 65-68° alone and on mixing with an authentic sample, and b. p. 128-129°/ 0.05 mm., 19.6 g. (40%) of crude 5-pentyloxy methyl-8-quinolinol, melting at 45-50°. Repeated crystallization from hexane yielded pure product, m.p. 52.5-53.5°.
Anal. Calc'd. for $C_{15}H_{19}NO_2$: C,73.47; H,7.75; N,5.71.
Found: C,73.29; H,7.68; N,5.75.
The crude 5-hydroxymethyl-8-quinolinol was purified by sublimation at 135°/0.1 mm. followed by recrystallization from benzene to afford XII melting at 139-140°.

5-Hexyloxymethyl-8-quinolinol (XVI)

In a similar manner, 5-chloromethyl-8-quinolinol hydrochloride and 1-hexanol gave the crude product, b.p. 150-155°/ 0.3 mm., m.p. 40-42° in a yield of 45%. Upon recrystallization from hexane the pure material melted at 42-43°.
Anal. Calc'd. for $C_{16}H_{21}NO_2$: C,74.13; H,8.11; N,5.40.
Found: C,74.09; H,7.98; N,5.44.

5-Heptyloxymethyl-8-quinolinol (XVII)

Similarly, 5-chloromethyl-8-quinolinol hydrochloride and 1-heptanol gave the pure product, m.p. 52-53° in a yield of 23%.
Anal. Calc'd. for $C_{17}H_{23}NO_2$: C,74.73; H,8.43; N,5.13.
Found: C,74.80; H,8.23; N,5.14.

5-Dimethylaminomethyl-8-quinolinol (XVIII)

Liquid dimethylamine (45 g., 1 mole) was added to ice-cooled hexane (250 ml.). To this stirred solution was introduced 5-chloromethyl-8-quinolinol hydrochloride (46 g., 0.2 mole) over a period of 10 minutes. The mixture was allowed to come to room temperature, stirred for 30 minutes, and then boiled for an additional 90 minutes. It was then cooled and diluted with ether. The precipitate which was formed, dimethylamine hydrochloride, was filtered amd washed with ether. The combined filtrate was washed with water and dried. After removal of the solvents, it gave 28.8 g. (72%) of XVIII, mp 100-105°. The product was purified by sublimation at 90°/0.1 mm. followed by recrystallization from ligroine (60-90°) to yield sample melting at 113-115°.
Anal. Calcd. for $C_{12}H_{14}N_2O$: C,71.29; H,6.93; N,13.86.
Found: C,71.28; H,6.92; N,13.82.

5-Diethylaminomethyl-8-quinolinol (XIX)

A mixture of 46 g. (0.2 mole) of 5-chloromethyl-8-quinolinol hydrochloride and a solution of 55 g. (0.75 mole) of diethylamine in 200 ml. of hexane was stirred and heated at reflux for 2 hours. After cooling the reaction mixture was poured into 1 l. of ether and the diethylamine hydrochloride which precipitated were filtered and washed with ether. The filtrate was concentrated by distilling the ether and the excess of diethylamine. The solid residue was crystallized from hexane, giving 41.3 g. (90%) of XIX, m.p. 69-71°. The product was purified by sublimation at 135°/0.1 mm. followed by recrystallization from hexane to afford crystals melting at 70-72°. [Lit. (13) m.p. 70-72.8]

N, N-Bis (8-hydroxy-5-quinolylmethyl) propylamine (XXVII)

A mixture of 23 g. (0.1 mole) of 5-chloromethyl-8-quinolinol hydrochloride, 30 g. (0.5 mole) of n-propylamine and 200 ml. of hexane was stirred at reflux for 2 hours. After cooling, the precipitated n-propylamine hydrochloride was filtered and washed with ether and benzene. Concentration of the filtrate gave as first crop 5.4 g. (29%) of crystals melting at 155-159°. Recrystallization from benzene raised the melting point to 158-160°.
Anal. Calcd. for $C_{23}H_{23}N_3O_2$: C,73.99; H,6.17; N,11.26. Mol. weight 373.
Found: C,74.50; 6.04; N,11.18. Mol. weight by titration with perchloric acid, 396.
Further concentration of the filtrate containing hexane gave several successive crops which melted over a wide range of temperature.

5-Di-n-propylaminomethyl-8-quinolinol (XX)

The product was prepared in a yield of 98% by reacting in a similar manner 5-chloromethyl-8-quinolinol hydrochloride with a hexane solution of di-n-propylamine, m.p. 83-84° (after sublimation at 100°/0.1 mm and recrystallization from hexane).
Anal. calcd. for $C_{16}H_{22}N_2O$: C,74.42; H,8.53; N,10.85.
Found: C,74.06; H,8.46; N, 10.74.

5-Di-n-butylaminomethyl-8-quinolinol (XXI)

In a similar manner 5-chloromethyl-8-quinolinol hydrochloride and di-n-butylamine in hexane gave XXI in a yield of 77%, mp. 69-70° (sublimation at 120°/0.1 mm followed by recrystallization from hexane).
Anal. Calcd. for $C_{18}H_{26}N_2O$: C,75.52; H,9.09; N,9.79.
Found: C,75.04; H,9.02; N,9.74.

5-(2-Hydroxyethoxymethyl)-8-quinolinol (XXII)

To a stirred ethylene glycol (248 g., 4 moles) dried earlier over molecular sieves was added 5-chloromethyl-8-quinolinol hydrochloride (46 g., 0.2 moles). After stirring for 4 hours at 120°, the mixture was cooled and poured into 2 l. of ether. The lower oily layer containing hydrochloride salt, was separated, washed with ether and then dissolved in water. The aqueous solution, after being made alkaline with sodium bicarbonate, gave 28 g. (64%) of XXII, mp 103-106°. Fractional distillation afforded a product boiling at 190-200°/0.1 mm. which was recrystallized from benzene, mp. 108-109°.
Anal. Calcd. for $C_{12}H_{13}NO_3$: C [illegible].75; H,5.94; N,6.39.
Found: C,65.74; H,5.52; N,6.34.

5-(7-Hydroxy-2,5-dioxaheptyl)-8-quinolinol (XXIII)

A mixture of 46 g. (0.2 mole) of 5-chloromethyl-8-quinolinol hydrochloride and 300 g. (2.8 mole) of anhydrous diethylene glycol was stirred at 120° for 4 hours. After cooling, the mixture was poured into 1200 ml. of water and then made alkaline with sodium bicarbonate. Extraction with ether gave, after removal of the solvent, 31 g. of a liquid containing a small amount of diethylene glycol. The liquid was dissolved in ether, anhydrous hydrogen chloride was passed through the solution and the precipitated hydrochloride salt was separated. The hydrochloride salt was then dissolved in water and the solution made alkaline with sodium bicarbonate. Extraction with ether gave 24.4 g. of an oil. The oil was dissolved in benzene and allowed to stand at 0° for several days. It gave 7.1 g. (13.5%) of crystals, melting at 56-58°. Sublimation at 150-160°/0.05 mm. followed by crystallization from benzene afforded pure sample m.p. 61-62°.
Anal. Calcd. for $C_{14}H_{17}NO_4$: C, 63.88; H,6.46; N,5.32.
Found: C,63.78; H,6.38; N,5.34.

5-(2-Methoxyethoxymethyl)-8-quinolinol (XXIV)

A mixture of 23 g. (0.1 mole) of 5-chloromethyl-8-quinolinol hydrochloride and 152 g. (2 moles) of ethylene glycol monomethyl ether was stirred at reflux temperature for 4 hours. The mixture was then cooled and poured into ether. The solid hydrochloride salt which precipitated was filtered and then dissolved in water. The solution was made alkaline with sodium bicarbonate and the solid which precipitated was filtered to afford 16 g. of the crude product, m.p. 55-60°. Distillation gave two main fractions: 1) b.p. 65 - 75°/0.1 mm, m.p. 58 - 60°, 3.2 g. of 8-quinolinol probably present as impurity in the starting chloromethyl compound, and 2) b.p. 137 - 142°/0.1 mm., m.p. 67 - 70°, 10 g. (43%) of XXIV. Repeated crystallization of the second fraction from heptane afforded pure sample, m.p. 70 - 71°.
Anal. Calcd. for $C_{13}H_{15}NO_3$: C,66.95; H,6.44; N,6.01. Found: C,66.94; H,6.41; N,5.97.

5-(2,5,8-Trioxanonyl)-8-quinolinol (XXV)

A mixture of 46 g. (0.2 mole) of 5-chloromethyl-8-quinolinol hydrochloride and 240 g. (2.0 moles) of diethylene glycol monomethyl ether was stirred and heated at 120 - 125° for 4 hours. The mixture was concentrated by distilling in vacuo the excess of diethylene glycol monomethyl ether. The residual product was treated with ether and the precipitated hydrochloride salt was separated by filtration and then dissolved in water. The aqueous solution was made alkaline with sodium bicarbonate and then extracted with ether. Distillation of the ether solution gave two main fractions: 1) B.p. 65 - 75°/0.2 mm., m.p. 56 - 60°, containing 8 -quinolinol and 2) b.p. 186 - 193°/0.2 mm., 29.5 g. (54%) of the crude polyether. The second fraction was redistilled to afford 15 g. of the pure XXV, b.p. 172 - 174°/0.05 mm., n_D^{24} 1.5742.
Anal. Calcd. for $C_{15}H_{19}NO_4$: C,64.98; H, 6.86; N,5.05.
Found: C,64.94; H,6.82; N,4.98.

5-(2,5,8.11-Tetroxadodecyl)-8-quinolinol (XXVI)

A mixture of 69 g. (0.3 mole) of 5-chloromethyl-8-quinolinol hydrochloride and 214 g. (1.3 mole) of triethylene glycol monomethyl ether was stirred and heated at 125 - 130° for 5 hours. A solid, insoluble in the mixture, was removed by filtration and washed with ether. The solid, hydrochloride salt, was dissolved in water and the aqueous solution made alkaline with sodium bicarbonate to yield 5.7 g. of 5-hydroxymethyl-8-quinolinol, m.p. 125 - 130°. The filtrate containing excess of triethylene glycol monomethyl ether was diluted with ether. The hydrochloride salt, which precipitated, was filtered, dissolved in water and the aqueous solution made alkaline with sodium bicarbonate. Extraction with ether gave 44 g. of an oil as the residual material, which was purified by distillation. Two main fractions

were collected: 1) b.p. 80 - 90°/0.3 mm., m.p. 56 - 60°, 5 g. of 8-quinolinol, and 2) b.p. 193 - 200°/0.1 - 0.2 mm., 26.3 g. (27.5%) of the polyether XXVI. The second fraction was redistilled to give pure sample, b.p. 200 - 206°/0.2 mm., n_D^{22} 1.5585.
Anal. calcd. for $C_{17}H_{23}NO_5$: C,63.55; H,7.17; N,4.36.
Found: C,63.42; H,7.09; N,4.40.

III. DISCUSSION

In this work the high purity of the synthesized compounds was particularly emphasized. This required the use of several purification methods in each preparation and the application of gas chromatography, as well as infrared and ultraviolet spectroscopic analyses for verification of the purity of the materials.

Because of these circumstances the yield of some synthesized products was low. Particularly this was the case for 5-substituted ethers and polyethers which were prepared by reacting 5-chloromethyl-8-quinolinol hydrochloride with alcohols or glycols probably containing traces of water. The desired products were admixed with a by-product 5-hydroxymethyl-8-quinolinol and the purification involved an elaborate procedure.

In the preparation of 5-substituted ethers and polyethers the alcoholic reagents were usually applied in an excess of the stoichiometric amount to serve as solvents for the produced products as well as the reaction medium, for heat transfer and dispersion of the starting insoluble chloromethyl compound.

Some of the new compounds besides being considered as potential corrosion inhibitors, may find application in other fields. For instance the 2- and 7-isopropyl-8-hydroxyquinoline and the ethers, 5-pentyloxy-, 5-hexyloxy-, and 5-heptyloxymethyl-8-quinolinol, because of the presence of a paraffinic chain in their molecules, are soluble in hydrocarbons and consequently in liquid fuels. These compounds contain also a phenolic group in their molecules and are potential antioxidants for fuels.

It is known (16) that some chelates are used as "Metal Deactivators" in gasoline because they form stable metal chelates with copper ions present in the fuel and this way prevent initiation of a free radical polymerization reaction which leads to gums.

The above new derivatives may have similar or better activity as fuel additives because of their solubility in gasoline and chelating properties.

IV. CONCLUSIONS

A series of new derivatives of 8-quinolinol was prepared. These compounds contain groups such as alkyl, hydroxy, alkoxy, amine and polyethylenoxy. These products are of interest for theoretical and practical applications.

V. RECOMMENDATIONS

1. The new derivatives are of interest as corrosion inhibitors and should be tested as such.

2. The new compounds, 5-substituted ethers derived from 8-quinolinol and 2 -, and 7-isopropyl-8-quinolinol should be tested as gasoline additives and compared with commercially available materials.

3. New compounds derived from 8-quinolinol should be synthesized to have at different positions of the molecule substituents similar to those attached to position 5 and prepared in this work. The physical properties and practical performance of the proposed compounds should be compared with those of the derivatives reported in this work to assess the effect of the position in the molecule on the overall properties.

VI. ACKNOWLEDGEMENT

The author is grateful to Mr. Melvin Swann for titrometric analyses, Miss Martha Adams for infrared and ultraviolet spectroscopic analyses, Mr. George Esposito for gas chromatographic analyses, Dr. George Kleinspehn for recording and consultation on nmr spectra, and Mr. M. LePera for drawings.

VII. BIBLIOGRAPHY

1. F. P. Dwyer and D. P. Mellor, Chelating Agents and Metal Chelates, Academic Press, New York, 1964, p. 118.

2. J. P. Phillips, Chem. Rev. 56, 272 (1956).

3. A. Kaufmann and E. Rothlin, Chem. Ber., 49, 578 (1916).

4. H. Gilman and S. M. Spatz, J. Am. Chem. Soc., 63, 1553 (1941).

5. F. Sorm and J. Sicher, Collection Czech. Chem. Commun. 14, 331 (1949).

6. L. J. Bellamy, The Infra-red spectra of complex molecules, Methuen and Co., ltd., London, 1954, p. 89.

7. M. Fileti, Gazz. Chim. Ital. 16, 121 (1886).

8. R. H. F. Manske and M. Kulka in Organic Reactions Vol. VII, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 59.

9. R. Long and K. Schofield, J. Chem. Soc., 3161 (1953).

10. G. P. Gibson, J. Chem. Soc., 127, 44 (1925).

11. E. Noelting and E. Traufmann, Chem. Ber. 23, 3663 (1890).

12. H. Zinner and H. Fiedler, Arch. Pharm., 291, 493 (1958).

13. J. H. Burckhalter and R. I. Leib, J. Org. Chem., 26, 4078 (1961).

14. Q. Fernando, W. W. L. Ludekens and K. Gwanasoorian, Anal. Chim. Acta, 14, 297 (1956).

15. R. Gopalchari and M. L. Dhar, J. Sci. Ind. Res., 19C, 233 (1961).

16. J. R. Lodwick, J. Inst. Of Petroleum, 50, 297 (1964).

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY *(Corporate author)* U. S. Army Coating and Chemical Laboratory Aberdeen Proving Ground, Maryland	2a REPORT SECURITY CLASSIFICATION 2b GROUP

3 REPORT TITLE
DERIVATIVES OF 8-QUINOLINOL

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Progress report

5 AUTHOR(S) *(Last name, first name, initial)*
Kolobielski, Marjan

6. REPORT DATE August 1966	7a. TOTAL NO. OF PAGES	7b NO. OF REFS

8a. CONTRACT OR GRANT NO. AMCMS CODE NO. 5016.11.844	9a. ORIGINATOR'S REPORT NUMBER(S) CCL #207
b. PROJECT NO. 1L013001A039	
c	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10 AVAILABILITY/LIMITATION NOTICES
Qualified requesters may obtain copies of this report from Defense Documentation Center. Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U.S. Army Materiel Command Washington, D. C. 20315

13. ABSTRACT

The overall objective of this project is the establishment of the relation of the hydrophilic-lipophilic ratios of chelating compounds and selected solvents to the corrosion inhibitory action of these compounds in various solvents. Derivatives of 8-quinolinol containing different substituents were selected as the chelates for the initial investigation of physical properties such as dissociation constants, stability constants, hydrophilic-lipophilic ratios and of their corrosion inhibitory action. The results obtained may also allow one to relate the effect on corrosion inhibition of the molecular structure of these derivatives. In this study the needed derivatives were prepared in high purity and their structure proved by the use of non-equivocal synthetic means. The majority of the compounds are new products derived from 8-quinolinol and containing groups such as alkyl, hydroxy, alkoxy, amine and polyethylenoxy. The new compounds besides being considered as corrosion inhibitors may in some cases be potential additives for liquid fuels as antioxidants and metal deactivators, and will be screened for such possibilities.

Unclassified
Security Classification

Unclassified
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Organic Synthesis Quinoline Derivatives Corrosion Inhibitors						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through
____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through
____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through
____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS), (S), (C), or (U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

Unclassified
Security Classification