47. N-*Substituted Quinolinium Ions. Part I. The Reactions between the* N-*Cyanoquinolinium Ion and Some Nucleophiles.*

By M. D. Johnson.

The reactions of the *N*-cyanoquinolinium ion with a number of nucleophiles are discussed with reference to the structure and stability of the products. Several nucleophiles, such as alkoxide, hydroxide, and t-butyl peroxide ions give stable 1,2-dihydroquinolines. The reaction with water is accompanied by the loss of a proton, to give a 1,2-dihydroquinoline. Other weak nucleophiles such as bromide and acetate ions do not give stable dihydroquinolines, but evidence is presented that dihydroquinolines are formed in small amounts is solution. The structure of the pseudo-base, 1-cyano-1,2-dihydro-2-hydroxyquinoline, is discussed in some detail.

The recent revival of interest in the reactions of *N*-substituted heterocyclic cations with nucleophiles has resulted from suggestions that *N*-substituted quinolinium ions are intermediates in electrophilic substitution in quinoline,[1,2] from the biological importance of reactions of the diphosphopyridine nucleotide,[3] and from the possibility of solving classical problems in this field by the use of modern techniques. However, little reliable information is available about the factors determining the position of attack or the equilibria involved in the formation of the dihydro-derivative. The present two papers are concerned with the structure and properties of the dihydro-compounds derived from one such heterocyclic cation, the *N*-cyanoquinolinium ion.

This ion was chosen because it was evident from the literature that the presence of strongly electron-withdrawing groups ($-T$) in the molecule,[4] and in particular on the heteroatom,[5] results in a reactive cation, and consequently in somewhat stable dihydro-derivatives. Moreover, it was hoped that the *N*-cyanoquinolinium ion would be a suitable model for the less readily isolated *N*-nitro-[6] and *N*-bromo-quinolinium ions which have been postulated as transient intermediates in the nitration and bromination of quinoline, respectively.

N-*Cyanoquinolinium Fluoroborate.*—Though the *N*-cyanoquinolinium ion has previously been isolated as the perchlorate,[7] none of its properties has been measured. The fluoroborate is much more easily prepared and handled than the perchlorate. It is stable in dry air, and indefinitely in a stoppered bottle. The *N*-cyanoquinolinium ion has an ultraviolet spectrum ($\lambda_{max.}$ 246, 328, 369 mμ; $\log_{10} \varepsilon$ 4·36, 3·96, 3·58) that is similar to that of the *N*-nitroquinolinium ion,[6] but is quite uncharacteristic of other simple *N*-substituted quinolinium ions (*e.g.*, *N*-methyl, $\lambda_{max.}$ 314 mμ), indicating a very strong conjugative interaction with the quinoline ring. The ion also shows a characteristic yellow-green fluorescence.

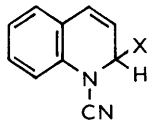
Reaction with strong nucleophiles. The *N*-cyanoquinolinium ion reacts very rapidly with a number of nucleophiles, *e.g.*, primary, secondary, and tertiary alkoxide, t-butyl peroxide, and hydroxide ions, or the conjugate base of 1-cyano-1,2-dihydro-2-hydroxyquinoline (I). In all cases the product is the corresponding 1,2-dihydroquinoline (II), (III), (I), and (IV), respectively.

All the compounds (I—IV) show strong absorption due to the CN groups at 2217—2227 cm.$^{-1}$ and give the protonated quinolinium ion on treatment with hydrochloric acid. In addition, 1-cyano-1,2-dihydro-2-hydroxyquinoline (I) shows a strong absorption at 3389

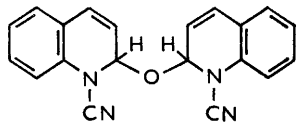
[1] Dewar and Maitlis, *J.*, 1957, 944.
[2] Brown and Harcourt, *J.*, 1959, 3451.
[3] Kosower, "The Enzymes," Academic Press, New York, 1960, Vol. II, Chapter 13.
[4] Decker and Kaufmann, *J. prakt. Chem.*, 1911, **84**, 425.
[5] McEwen and Cobb, *Chem. Rev.*, 1955, **55**, 511.
[6] Foster, Ph.D. Thesis, London, 1954.
[7] Mumm and Ludwig, *Annalen*, 1934, **514**, 34.

cm.$^{-1}$ due to the hydroxyl group, and the peroxy-ether (III) shows strong absorption at 865 cm.$^{-1}$ usually associated with the peroxide bond.[8] The infrared spectra of all four compounds are otherwise very similar. The ultraviolet spectra of compounds (I), (II), and (IV) are almost identical ($\lambda_{max.}$ 226, 262, 304 mμ; $\log_{10}\varepsilon$ * 4·55, 3·85, 3·42) and that of the peroxy-ether (III) is very similar except for a very slight shift of the second band ($\lambda_{max.}$ 265 mμ). However, the spectra are sufficiently similar to indicate that the compounds all have similar structure.

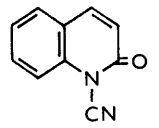
The proof of the position of the group X depends mainly on that of the t-butylperoxy-group in the ether (III). An ethereal solution of this ether, on treatment with triethylamine or piperidine, undergoes cleavage of the peroxide bond and loss of the α-hydrogen



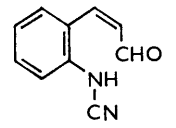
(I) X = OH
(II) X = OAlk
(III) X = O·OBu^t
(VII) X = Br
(VIII) X = OAc



(IV)



(V)



(VI)

atom to form crystalline 1-cyano-2-quinolone (V). This compound can be readily hydrolysed to 2-hydroxyquinoline. In view of the stability of the alkyl ethers (II) to the same reagent, and of the coloured products obtained from the *N*-cyanoquinolinium ion with piperidine, it is most unlikely that the reaction is accompanied by a shift of the t-butylperoxy-group around the ring.

Unfortunately neither the quinolone (V) nor 2-hydroxyquinoline can be obtained in good yield by direct oxidation of the hydroxy-compound (I) with alkaline potassium ferricyanide. Under such conditions, only 16% of 2-hydroxyquinoline is obtained, the other products being the ether (IV) and degradation products also obtained in the absence of potassium ferricyanide. That the compound (I) is stable to atmospheric oxidation is of interest because of the ready oxidation of many other dihydroquinolines.

Reaction with other nucleophiles. The *N*-cyanoquinolinium ion reacts rapidly with the phenoxide ion, but the product is not a simple dihydroquinoline. By analogy with the reactions of other *N*-substituted quinolinium ions, the product is probably derived from the open chain form (VI) of the compound (I).

The reaction with weaker nucleophiles is much more difficult to demonstrate because of the instability of the corresponding dihydroquinoline derivatives. However, it is important to determine the extent of reaction, and if possible the position of attack of the nucleophile. The reaction between quinoline and cyanogen bromide has long been known [9] but in no case has crystalline *N*-cyanoquinolinium bromide or the corresponding covalent dihydroquinoline (VII) been obtained. However, since the product of the reaction reacts rapidly with water to give the hydroxy-compound (I), or the ether (IV), there is little doubt that it contains, or rapidly furnishes, the *N*-cyanoquinolinium ion. Similarly, attempts to prepare the acetate or its corresponding covalent dihydroquinoline (VIII) have been unsuccessful. In view of the low nucleophilicity of the acetate ion in a large number of other reactions,[10] this is to be expected; however, several attempts were made to acetylate the compound (I).

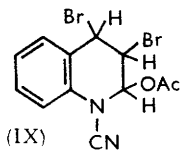
* $\log_{10}\varepsilon$ here refers to the molar extinction coefficients of (I) and (II). The values for the ether (IV) are approximately twice those shown.

[8] Philpotts and Thain, *Analyt. Chem.*, 1952, **24**, 638.
[9] von Braun, *Ber.*, 1900, **33**, 1438.
[10] Swain and Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 141.

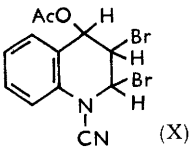
Keten reacts with the hydroxy-compound (I) in acetone, giving a yellow-green solution with the characteristic fluorescence of the *N*-cyanoquinolinium ion. Evaporation under reduced pressure gave first a bright red solution and finally a deep red oil. The yellow-green solution had $\lambda_{max.}$ 335 mμ, almost identical with that observed for a solution of *N*-cyanoquinolinium fluoroborate in acetone in the presence of a trace of acetate ion, after being kept for 8 minutes. The fluoroborate solution showed the same characteristic behaviour on evaporation of the acetone. In methanol, keten and the hydroxy-compound (I) gave almost entirely the methoxy-compound (II), also obtained by reaction of the *N*-cyanoquinolinium ion with methanol in the presence of a base such as triethylamine. No reaction between the hydroxy-compound and keten in ether was observed.

These experiments show that the hydroxyl group of compound (I) can be acetylated, but that the dihydroquinoline derivative breaks down into the *N*-cyanoquinolinium ion and acetate ion; the former can then react further with the solvent or its conjugate base liberated by the acetate ion. In acetic anhydride the *N*-cyanoquinolinium ion is slowly decomposed to a more stable quinolinium ion ($\lambda_{max.}$ 314 mμ). The initial ultraviolet spectrum of the system closely resembles that of the *N*-cyanoquinolinium ion in perchloric acid, and during the reaction an isosbestic point is maintained. The hydroxy-compound (I) is stable in the same solvent and it is therefore assumed that the covalent 2-acetoxy-1-cyano-1,2-dihydroquinoline, if not ionised, would also be stable in the same solution. The character of the initial spectrum and the observation of an isosbestic point thus show that 2-acetoxy-1-cyano-1,2-dihydroquinoline, if present at all, must be in low concentration in rapid equilibrium with the ionic species.

It is possible to demonstrate that some weak nucleophiles can add to the *N*-cyanoquinolinium ion to give a finite amount of the dihydroquinoline in solution. In the following paper the reactions of the 3,4-double bonds of some 1,2-dihydroquinolines are described. It is shown that the elements of bromine or bromine acetate are rapidly and irreversibly added across the 3,4-double bonds under suitable conditions, whereas the *N*-cyanoquinolinium ion does not react with bromine in concentrated perchloric acid. When *N*-cyanoquinolinium fluoroborate is added to a solution of bromine in acetic anhydride containing a large excess of sodium acetate, a crystalline tetrahydroquinoline derivative, either (IX) or (X), is formed in good yield. This tetrahydroquinoline can be



(IX)



(X)

formed in four possible ways: by addition of bromine to the initially formed 2(or 4)-acetoxy-1-cyano-1,2(or 1,4)-dihydroquinoline, or by addition of bromine acetate to the initially formed 2(or 4)-bromo-1-cyano-1,2(or 1,4)-dihydroquinoline. Thus the determination of the exact structure of the tetrahydroquinoline derivative (IX) or (X) would be of little help in determining the nature of the initially formed dihydroquinoline derivative. Since little is known of the addition of bromine or bromine acetate to 1,4-dihydroquinoline derivatives, the possibility that the rates of addition control the product, and hence the apparent first formed dihydroquinoline, must also be considered. However, whichever mechanism operates, it can be said that one of the weaker nucleophiles (Br^- or OAc^-) must necessarily have formed a finite amount of the dihydroquinoline derivative.

Reaction with water. The *N*-cyanoquinolinium ion reacts rapidly with water to give the hydroxy-compound (I). In order to determine whether this reaction was due to hydroxide ion or to water, it was carried out in solutions containing various concentrations of acid. In 0·1M-fluoroboric or -perchloric acid the hydroxy-compound is formed immediately; this is shown by isolation of the hydroxy-compound (I) from the ethereal

phase after *N*-cyanoquinolinium fluoroborate had been shaken with 0·1M-fluoroboric acid and ether for 15 seconds. Similarly, when a solution of the *N*-cyanoquinolinium ion in 60% perchloric acid is diluted with water to 0·12M-perchloric acid, the ultraviolet spectrum shows an immediate change to that characteristic of the hydroxy-compound (I) ($\lambda_{max.}$ 303, 262 mμ; $\log_{10}\varepsilon$ 3·42, 3·84), and a subsequent slower change to the protonated quinolinium ion. If the solution in 60% perchloric acid is diluted to 1·0M, then the ultraviolet spectrum initially resembles that of the *N*-cyanoquinolinium ion, and this changes fairly rapidly into that of the protonated quinolinium ion. Isosbestic points are maintained throughout the reaction in 1·0M-perchloric acid and the slower reaction in 0·12M-perchloric acid. These results show that the lower limit for appreciable formation of the hydroxy-compound (I) lies between 0·12 and 1·0M-perchloric acid and, because of the fast rate of the reaction, it must be ascribed to water rather than to the hydroxide ion, despite the low nucleophilicity of the former reagent.

Comparison with previous work. The reaction of nucleophiles with other quinolinium ions has been discussed elsewhere.[2,11] It seems generally accepted that strong nucleophiles attack the 2-position whereas weak nucleophiles attack the 4-position, though the evidence in favour of this view is not entirely unambiguous. Thus most of the evidence for the assignment of the position of the nucleophilic group is based on the results of chemical reactions in solution [12] and, since the relevant products are frequently in rapid equilibrium with the ionic species, there is always the possibility that kinetic control of subsequent reactions may give rise to products derived from a dihydroquinoline initially present only in minute yield. This has been shown to be the case in the dehydrogenation of dihydroquinoline derivatives obtained from *N*-benzylquinolinium ions and the anions derived from some ketones.[13] The dehydro-compound obtained depends upon the reagent used; thus with *NN*-dimethyl-*p*-nitrosoaniline as the dehydrogenating agent, the 1,4-dehydro-compound is obtained, but with potassium permanganate as the dehydrogenating agent the 1,2-dehydro-compound is obtained, both in good yield. Such may also be the case with the oxidation of the products of reaction of hydroxide and cyanide ions with the *N*-methylquinolinium ion. Theoretical arguments have been put forward to explain the generally accepted view of orientation of nucleophilic addition; thus Brown and Harcourt have calculated that the lowest electron density is at the 2-position, and the lowest nucleophilic localisation energy is associated with the 4-position. They point out that, since a strong nucleophile will require little rearrangement of the π-electrons in the transition state, it will attack the position of least electron density, *i.e.*, the 2-position. Similarly, since a weak nucleophile will require considerable rearrangement of the π-electrons in the transition state, it will attack that position where the nucleophilic localisation energy is a minimum, *i.e.*, the 4-position.

The reactions described in the present work differ from those discussed above in that they are effectively irreversible under normal conditions. The structures of the products can therefore be reliably determined by both physical and chemical methods. Since all the dihydroquinolines were formed by attack of the nucleophile at the 2-position, no definite statements can be made about the stability of the corresponding 1,4-dihydroquinolines. However, as the dihydroquinolines (II), (III), and (IV) are extremely stable in solution, it is quite likely that the corresponding 1,4-dihydroquinolines would also be fairly stable. This is supported by observations that, in other quinolinium systems, the 1,4-dihydroquinolines are sufficiently stable for products to be derived from them, and since the replacement of, say, a methyl group on the heteroatom by the cyano-group provides considerable stability for the 1,2-dihydroquinoline, it would be expected to effect a similar increase in stability of the 1,4-dihydroquinoline derivative. If this is true, then it can be said that strong nucleophiles such as hydroxide and t-butyl peroxide ion, and

[11] Bradley and Jeffrey, *J.*, 1954, 2770.
[12] Kaufmann and Albertini, *Ber.*, 1909, **42**, 3776; Decker, *Ber.*, 1891, **24**, 690.
[13] Kröhnke and Vogt, *Annalen*, 1956, **600**, 228.

weak nucleophiles such as water, attack the 2-position faster than they attack the 4-position. In this case the results do not agree with Brown and Harcourt's calculations. If it is assumed that the *N*-cyanoquinolinium ion is an extreme case which lies outside the limits of the calculations, then the discrepancies might be resolved by extending the calculations by using slightly higher values of the coulomb parameters involved. However, this would lead to the result that the π-electron densities and the nucleophilic localisation energies are both lowest at the 4-position, which is still not in agreement with experiment.

If, on the other hand, the corresponding 1,4-dihydroquinolines are extremely unstable, then all that can be said is that the more stable dihydroquinoline is being formed, without reference to reactivity or to any initial unstable products. The more stable product would therefore be expected to be that obtained by attachment of the nucleophile to the position of lowest nucleophilic localisation energy. Since the calculations suggest that this is the 4-position, they are not in accord with the results obtained.

Some estimate of the relative nucleophilicities of the anions, other than the broad classification, weak or strong, is also desirable. In principle the estimation of relative nucleophilicities in this system should not be difficult because the reactions are effectively irreversible, and so product yields should be directly proportional to the individual rates of reaction. However, other factors complicate such an analysis, the complications being characteristic of any pair of nucleophiles chosen. The comparison of hydroxide and ethoxide ions, for example, is impracticable because of the base-catalysed exchange of OH by OEt with the hydroxy-compound (I) in ethanol. However, it can be shown that ethoxide ion is a stronger nucleophile towards the *N*-cyanoquinolinium ion than is the t-butyl hydroperoxide ion, for only the ethoxy-compound (II) can be recovered from an equimolar solution with sodium t-butyl peroxide and sodium ethoxide in ethanol. Ethanol itself does not give the same product. This result is of interest because previous measurements of relative nucleophilicity involving hydroperoxide anions have shown the alkoxide ions to be less reactive.[14] The isolation, by Rieche *et al.*,[15] of 1,2-dihydro-1-methyl-6,8-dinitro-2-t-butylperoxyquinoline from a solution of the corresponding ethoxy-compound and t-butyl hydroperoxide in ethanol is therefore almost certainly due to the fairly rapid ionisation of the ethoxy-compound and the much greater acidity of t-butyl hydroperoxide than of ethanol, resulting in a gradual replacement of ethoxide ions by t-butyl hydroperoxide ions in solution, and hence in the formation of the dihydro-2-t-butoxyquinoline in preference to the 2-ethoxy-compound.

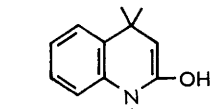
Structure of 1-*Cyano*-1,2-*dihydro*-2-*hydroxyquinoline.*—The structure of the heterocyclic pseudo-bases, of which the hydroxy-compound (I) is an example, has been the subject of much speculation. In particular the possibility of its existence as the open-chain amino-aldehyde [16] (VI) has frequently been considered. The absence of any carbonyl absorption in the infrared spectrum of the crystalline material suggests that the open-chain form is absent in the solid state, and the identity of the ultraviolet spectra of the hydroxy-compound (I) and the methoxy-compound (II) for which no such tautomerism is possible, suggests that the open-chain form is absent in solution. This is supported by the absence of any exchange of methoxyl for hydroxyl in a solution of the hydroxy-compound (I) in anhydrous methanol at room temperature, or on warming for a short time. It is probable that exchange would occur if the open-chain form were present in significant amounts. In fact, rapid exchange does occur in the presence of a basic catalyst such as triethylamine. Under such conditions the open-chain form is a very likely intermediate, for in aqueous alkali an irreversible reaction takes place in which the products are almost certainly derived from the open-chain form. This view is supported by the absence of

[14] Wiberg, *J. Amer. Chem. Soc.*, 1955, **77**, 2519; Jencks and Carriuolo, *ibid.*, 1960, **82**, 1778; Baddeley, *Ann. Reports*, 1955, **52**, 150.
[15] Rieche, Schmitz, and Dietrich, *Chem. Ber.*, 1959, **92**, 2239.
[16] Roser, *Annalen*, 1893, **272**, 222.

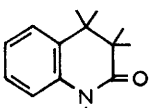
exchange of ethoxyl for methoxyl when the methoxy-compound (II) is treated with 0·1M-sodium ethoxide or triethylamine in ethanol, thus ruling out the mechanism involving direct bimolecular substitution. Exchange of methoxyl for hydroxyl does occur when the hydroxy-compound (I) is heated for some time in anhydrous methanol, but this probably proceeds by the unimolecular mechanism involving formation of the *N*-cyanoquinolinium ion as an intermediate.

These results are in striking contrast to those observed by Beke and Szántay [17] for the pseudo-base, 2-(2,4-dinitrophenyl)-1,2-dihydro-1-hydroxyisoquinoline. This pseudo-base is quantitatively converted in hot aqueous dioxan into the corresponding open-chain form, but the base-catalysed etherification does not proceed through this open-chain form; ionisation of the pseudo-base is relatively fast and provides a preferable path to the ether. The hydroxy-compound (I), when heated in aqueous dioxan or in water, remains unchanged and may be satisfactorily recrystallised in this way.

One other possible structure for the hydroxy-compound (I) must also be considered. This is the isomer (XII) formed by the transfer of a proton from the 2- to the 4-position, as suggested by Seeley *et al.*[18] for the corresponding cyano-compound. This compound would be the enolic form (XII) of *N*-cyanohydrocarbostyril (XIIa) and would almost certainly give hydrocarbostyril on acidic or basic hydrolysis; no hydrocarbostyril is



(XII)



(XIIa)

obtained. The absence of a carbonyl group absorption in the infrared spectrum of the hydroxy-compound (I) confirms the absence of the *N*-cyanohydrocarbostyril.

Experimental

1-*Cyanoquinolinium Fluoroborate.*—1-Cyano-1,2-dihydro-2-hydroxyquinoline (3·90 g., 0·0026 mole) was dissolved in fluoroboric acid (39 ml.; "commercial" 42%) at 45°, rapidly cooled to 0°, and then slowly cooled to −80°. After ½ hr. the crystalline 1-*cyanoquinolinium fluoroborate* was filtered off, washed with ether, and dried *in vacuo*. It had m. p. 160—163° (decomp.) (yield, 4·22 g., 72%) (Found: C, 49·4; H, 3·5; N, 12·1. $C_{10}H_7BF_4N_2$ requires C, 49·6; H, 2·9; N, 11·6%).

1-*Cyano*-1,2-*dihydro*-2-*hydroxyquinoline.*—(*a*) Potassium cyanide (65 g., 1 mole) in water (250 ml.) was added with stirring in 1 hr. to bromine (160 g., 1 mole) and water (750 ml.), the temperature being kept below 20°.[19] To this solution was added quinoline (271 g., 2·1 moles; "synthetic;" B.D.H), and the mixture was stirred for 3 hr. The solid was filtered off and ground as a paste with 0·1M-hydrochloric acid until the aqueous phase had pH ~2. The solid was then filtered off, washed with 0·1M-hydrochloric acid and water, and dried *in vacuo*. The yield was 129 g. (75%), and the m. p. 106—107° (decomp.) (from acetone, benzene, chloroform, water, or nitrobenzene) (Found: C, 69·3; H, 5·3; N, 15·7. Calc. for $C_{10}H_8N_2O$: C, 69·7; H, 4·7; N, 16·3%).

(*b*) 1-Cyanoquinolinium fluoroborate (1·2 g.) was added to 0·1M-perchloric acid (100 ml.) and ether (100 ml.). The mixture was shaken for 20 sec. and the ethereal phase was separated, washed with water, and dried (Na_2SO_4). On evaporation to dryness, the product was pure 1-cyano-1,2-dihydro-2-hydroxyquinoline identical with that described above (0·76 g., 80%).

1-*Cyano*-1,2-*dihydro*-2-*methoxyquinoline.*—Methanol (1·5 g., 0·047 mole) and triethylamine (1·32 g., 0·013 mole) were mixed and added with stirring to 1-cyanoquinolinium fluoroborate (3·16 g., 0·013 mole). After 5 min. ether (50 ml.) was added and stirring was continued for a further 5 min. The solution was filtered and washed with 0·1M-sodium hydroxide until the

[17] Beke and Szántay, *Annalen*, 1961, **640**, 127.
[18] Seeley, Yates, and Noller, *J. Amer. Chem. Soc.*, 1951, **73**, 772.
[19] *Org. Synth.*, Coll. Vol. II, 1960, p. 150.

washings were no longer yellow, then washed with water and dried (Na_2SO_4). The ether was distilled off and the residue recrystallised from light petroleum (b. p. 40—60°) at −80°, giving 1-*cyano*-1,2-*dihydro*-2-*methoxyquinoline* (0·88 g., 36%), m. p. 49—50° (Found: C, 71·5; H, 5·9; N, 15·8. $C_{11}H_{10}N_2O$ requires C, 72·0; H, 5·4; N, 15·1%).

The following were prepared similarly. 1-*Cyano*-2-*ethoxy*-1,2-*dihydro*-, m. p. 33—34° (Found: C, 72·0; H, 6·5; N, 13·9. $C_{12}H_{12}N_2O$ requires C, 72·0; H, 6·1; N, 14·0%), 1-*cyano*-1,2-*dihydro*-2-*isopropoxy*-, m. p. 54—55·5° (Found: C, 72·6; H, 6·9; N, 13·15. $C_{13}H_{14}N_2O$ requires C, 72·9; H, 6·6; N, 13·1%), and 1-*cyano*-1,2-*dihydro*-2-*t*-*butoxy*-*quinoline*, m. p. 88—89° (Found: C, 74·4; H, 7·3; N, 12·4. $C_{14}H_{16}N_2O$ requires C, 73·7; H, 7·1; N, 12·3%).

1-*Cyano*-1,2-*dihydro*-2-*t*-*butylperoxyquinoline*.—(*a*) This peroxide was prepared as described above for the methoxy-compound, but from t-butyl hydroperoxide. It had m. p. 85·5—86·5° (Found: C, 69·4; H, 6·9; N, 11·6. Calc. for $C_{14}H_{16}N_2O_2$: C, 68·8; H, 6·6; N, 11·5%). (*b*) 1-Cyano-1,2-dihydro-2-hydroxyquinoline (0·5 g.) and t-butyl hydroperoxide (0·5 g.) in ether (20 ml.) were treated with the boron trifluoride–ether complex (1 drop). The ethereal solution was filtered and the ether was distilled off. The residue recrystallised from light petroleum (b. p. 60—80°) to give the pure peroxide (0·54 g., 76%).

1-*Cyano*-2-*quinolone*.—1-Cyano-1,2-dihydro-2-t-butylperoxyquinoline (0·15 g.) was treated in ether (10 ml.) with triethylamine or piperidine (0·2 ml.) for 2 hr. The precipitate was washed with ether and on recrystallisation from ethanol had m. p. 179—180° (0·09 g., 87%) (Found: C, 71·3; H, 4·1; N, 17·1. Calc. for $C_{10}H_6N_2O$: C, 70·6; H, 3·55; N, 16·5%).

2-*Hydroxyquinoline*.—1-Cyano-2-quinolone (0·06 g.) was refluxed with sodium hydroxide (0·1 g.) in methanol (5 ml.) for 10 min. The solution was filtered and the filtrate was diluted with water (50 ml.), acidified to pH 3, and extracted with ether. The ethereal solution was dried (Na_2SO_4) and evaporated to dryness. The product (0·046 g., 90%) was shown to be 2-hydroxyquinoline by its mixed m. p. (198—199°) and infrared spectrum.

Di-(1-*cyano*-1,2-*dihydro*-2-*quinolyl*) *Ether*.—Triethylamine (1·3 ml., 0·01 mole) was added to a mixture of 1-cyanoquinolinium fluoroborate (2·42 g., 0·01 mole) and 1-cyano-1,2-dihydro-2-hydroxyquinoline (1·72 g., 0·01 mole) with stirring. After 3 min. ethyl alcohol (50 ml.) was added and the precipitate of di-(1-cyano-1,2-dihydro-2-quinolyl) ether was filtered off. After recrystallisation from nitrobenzene it had m. p. 136—137° (yield 1·89 g., 58%) (Found: C, 73·8; H, 4·8. Calc. for $C_{20}H_{14}N_4O$: C, 73·7; H, 4·3%).

Oxidation of 1-*Cyano*-1,2-*dihydro*-2-*hydroxyquinoline*.—1-Cyano-1,2-dihydro-2-hydroxyquinoline (1 g.) was added slowly with stirring to a solution of potassium ferricyanide (6·8 g.) and sodium hydroxide (1·6 g.) in water (20 ml.). The resulting suspension was filtered. The solid was washed with ethanol, dried *in vacuo*, and identified by mixed m. p. and infrared spectrum as di-(1-cyano-1,2-dihydro-2-hydroquinolyl) ether (0·15 g., 16%). The filtrate was acidified to pH *ca.* 10 and extracted with ether. The ethereal extract was dried (Na_2SO_4) and evaporated to dryness, to give 2-hydroxyquinoline (0·14 g., 16%). The aqueous phase after the ether extraction was acidified to pH 3 and again extracted with ether. This ethereal extract gave an unidentified product identical with that obtained from treatment of 1-cyano-1,2-dihydro-2-hydroxyquinoline with alkali in the absence of potassium ferricyanide.

Reaction of 1-*Cyanoquinolinium Fluoroborate with Phenoxide Ion*.—Phenol (1·31 g., 0·014 mole) and triethylamine (1·32 g., 0·013 mole) were mixed and added to 1-cyanoquinolinium fluoroborate (3·16 g., 0·013 mole) with stirring. After 5 min., light petroleum (b. p. 40—60°) (25 ml.) was added and stirring was continued for a further 5 min. The mixture was filtered and the filtrate was dried (Na_2SO_4) and cooled to −80°; a colourless oil separated. The petroleum was decanted and the oil dried *in vacuo*. The infrared spectrum of the oil showed none of the characteristics of dihydroquinolines and was not investigated further.

Reaction of 1-*Cyanoquinolinium Fluoroborate with Acetate Ion*.—Attempts to prepare 2-acetoxy-1-cyano-1,2-dihydroquinoline from *N*-cyanoquinolinium fluoroborate and acetic acid by the method described for the methoxy-compound were unsuccessful; only unchanged 1-cyanoquinolinium fluoroborate and 1-cyano-1,2-dihydro-2-hydroxyquinoline were isolated.

Acetylation of 1-*Cyano*-1,2-*dihydro*-2-*hydroxyquinoline*.—(*a*) Keten (generated from a lamp) was passed through a solution of 1-cyano-1,2-dihydro-2-hydroxyquinoline in acetone. After ~7 min. the solution had become yellow green and had $\lambda_{max.}$ 336 mμ 10 min. later. On evaporation under reduced pressure, an unidentified red solution and finally a deep red oil were obtained. The oil showed a strong band for a carbonyl group, but no other infrared characteristics of the expected dihydroquinoline. A solution of 1-cyanoquinolinium fluoroborate in

acetone saturated with sodium acetate had $\lambda_{max.}$ 333 mμ eight min. after mixing. The maximum drifted slowly to longer wavelengths.

(*b*) Keten was passed through a solution of 1-cyano-1,2-dihydro-2-hydroxyquinoline in anhydrous methanol for ½ hr. The methanol was removed under reduced pressure and the residue, after recrystallisation from light petroleum (b. p. 40—60°), was shown by mixed m. p. and infrared spectrum to be pure 1-cyano-1,2-dihydro-2-methoxyquinoline.

2(*or* 4)-*Acetoxy*-3,4(*or* 2,3)-*dibromo*-1-*cyano*-1,2,3,4-*tetrahydroquinoline*.—*N*-Cyanoquinolinium fluoroborate (2·42 g., 0·01 mole) was added to a freshly prepared solution of bromine (1·60 g., 0·01 mole) in acetic anhydride saturated with sodium acetate. After ~1 min. the solution was poured into water, stirred for ½ hr., and extracted with ether. The extract was washed with 0·1M-sodium hydroxide until the washings were no longer yellow, then with water, and dried (Na_2SO_4). The residue on evaporation was partially taken up in acetone, white crystals being filtered off and dried *in vacuo*. This product had m. p. 129° (decomp.) (0·92 g., 26%) (Found: C, 38·6; H, 3·1; N, 7·7. Calc. for $C_{12}H_{10}Br_2N_2O$: C, 38·6; H, 2·7; N, 7·5%).

Comparison of Reactivity of Ethoxide and t-Butyl Hydroperoxide Ions.—Sodium (0·23 g., 0·01 mole) was dissolved in absolute ethanol (50 ml.). t-Butyl hydroperoxide (0·45 g., 0·005 mole) was then added, followed immediately by *N*-cyanoquinolinium fluoroborate (0·51 g., 0·0021 mole). After 2 min. water was added and the solvent was extracted with chloroform. The chloroform solution was washed with water, dried (Na_2SO_4), and evaporated to dryness. The product, after recrystallisation from light petroleum (b. p. 60—80°), had m. p. 33—34° and was shown by mixed m. p. and infrared spectrum to be 1-cyano-2-ethoxy-1,2-dihydroquinoline. No 2-hydroxyquinoline or 1-cyano-2-quinoline was obtained from the aqueous phase.

Reaction of 1-*Cyano*-1,2-*dihydro*-2-*hydroxyquinoline with Methanol*.—1-Cyano-1,2-dihydro-2-hydroxyquinoline (1 g.) was dissolved in anhydrous methanol and kept at 25° for 60 hr. The product after evaporation of the methanol at <25° was unchanged 1-cyano-1,2-dihydro-2-hydroxyquinoline. When the experiment was repeated at the b. p. of methanol for 8 hr., the product was shown by its infrared spectrum to be mainly 1-cyano-1,2-dihydro-2-methoxyquinoline; the crude product was dissolved in ether and washed with 0·1M-sodium hydroxide and then with water, and dried (Na_2SO_4); working up the ethereal solution gave pure 1-cyano-1,2-dihydro-2-methoxyquinoline (0·85% g., 80%). The experiment was repeated in the presence of triethylamine (0·4 g.) for ½ hr. at 25°: the product was pure 1-cyano-1,2-dihydro-2-methoxyquinoline (0·96 g., 90%).

Reaction of 1-*Cyano*-1,2-*dihydro*-2-*methoxyquinoline with Ethanol*.—1-Cyano-1,2-dihydro-2-methoxyquinoline (0·18 g.) was dissolved in 0·1M-ethanolic sodium ethoxide (10 ml.). After 5 min. at 25° the solution was poured into water (400 ml.) and extracted with chloroform. The chloroform solution was washed with 0·1M-hydrochloric acid and water and dried (Na_2SO_4). On evaporation the product was unchanged 1-cyano-1,2-dihydro-2-methoxyquinoline. The acid washings were made alkaline with potassium hydrogen carbonate solution and extracted with ether. The ethereal solution afforded pure quinoline. When the experiment was carried out with M-sodium ethoxide for 15 min., no 1-cyano-1,2-dihydro-2-methoxyquinoline was obtained, but there was almost quantitative recovery (91%) as quinoline. When the experiment was carried out with triethylamine (0·3 g.) in ethanol for 30 min., only unchanged 1-cyano-1,2-dihydro-2-methoxyquinoline was obtained.

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