Anal. Calcd. for $C_9H_9N_3O_2$: C, 56.53; H, 4.74. Found: C, 56.61; H, 4.76.

3-Amino-2-(1-hydroxyethyl)-4(3*H*)-quinazolinone (IVf).—The solution of 24 g. of IIIc and 8.4 g. of anhydrous hydrazine in 2 l. of methanol was refluxed for 24 hr. and then allowed to stand at room temperature for 2 days, after which the solvent was distilled *in vacuo*. The residue was recrystallized from methylene chloride–hexane to give a quantitative yield (25 g.) of IVf, m.p. 108–110°. Infrared (in $CHCl_3$): 3450 and 3330 cm.$^{-1}$ (-NH_2); 1678 cm.$^{-1}$ (carbonyl group); 1605 cm.$^{-1}$ (—C═N—); 1034 cm.$^{-1}$ (-OH). Ultraviolet: λ_{max} 222 mμ (ϵ 24,000); 274 (6000); 305–306 (3500); and 316–317 (3000).

Anal. Calcd. for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40. Found: C, 58.71; H, 4.98.

2-Hydroxymethyl-1-methyl-4(1*H*)-quinazolinone (Va).—The suspension of 16 g. of IIIb in 1000 ml. of methanol was saturated with ammonia at room temperature, which resulted in a solution that was left to stand for 1 week. It was then evaporated *in vacuo*, and the solid residue recrystallized from methanol to give 5 g. of Va, m.p. 178–180°. Infrared (in $CHCl_3$): 3360 and 1078 cm.$^{-1}$ (-OH); 1653 cm.$^{-1}$ (carbonyl); 1603 cm.$^{-1}$ (>C═N—); 1528 cm.$^{-1}$ (Ar—CO—N═C—). Ultraviolet: λ_{max} 230 mμ (ϵ 16,500); 269 (4300); 276–277 (4500); 306–307 (6200); 317 (7900).

Anal. Calcd. for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.29; N, 14.73. Found: C, 63.46; H, 5.07; N, 14.96.

2-(1-Hydroxyethyl)-1-methyl-4(1*H*)-quinazolinone (Vb).—The suspension of 10.2 g. of IIId in 500 ml. of methanol was saturated with ammonia at room temperature, and the resulting solution left to stand for 1 week. It was then evaporated to dryness and the residue recrystallized from methanol to give 7.6 g. of Vb, m.p. 155–157°. Infrared (in $CHCl_3$): 3400 and 1088 cm.$^{-1}$ (-OH); 1648 cm.$^{-1}$ (carbonyl); 1605 cm.$^{-1}$ (>C═N—); 1535 cm.$^{-1}$ (Ar—CO—N═C—). Ultraviolet: λ_{max} 230 mμ (ϵ 16,600); 267 (4150); 276 (4350); 306 (8700); 314–315 (7750).

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.96; H, 5.80; N, 13.72.

Acknowledgment.—We are indebted to Dr. A. Steyermark for the microanalyses and to Mr. S. Traiman for the infrared spectra.

The Aromatization of Dihydroquinolines by Loss of the Elements of a Hydrocarbon[1]

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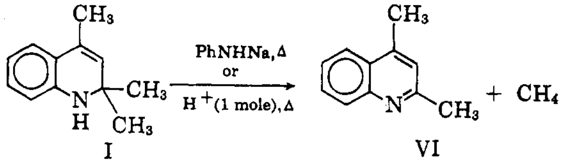
The aromatization of the hydrochloride of 2,2,4-trimethyl-1,2-dihydroquinoline has been carried out in solution and as the pure molten salt. In solution the reaction is initiated by *t*-butyl peroxide and catalyzed by β-naphthalenethiol. Eight quinoline products have been identified in the reaction without solvent. These products and the results in solution are consistent with the free-radical chain reaction mechanism proposed.

There exists a number of examples of reduced aromatic systems which are aromatized by loss of hydrogen and an alkyl group. One of the most familiar is the formation of Diels hydrocarbon involving the loss of two angular methyl groups from a steroid skeleton. Most of these aromatizations occur with reagents commonly associated with homolytic bond cleavage; however, there are examples of aromatizations of heteroaromatic systems which are subject to acid or base catalysis. Two reactions studied extensively by Elderfield are the loss of RH from a 2,2-disubstituted benzimidazoline or a 2,2-disubstituted benzothiazoline. Here no acid catalysis was observed, perhaps, as suggested by Elderfield, because these ring systems are unstable to acid. However, strong base catalysis has been observed in both reactions and a mechanism with a carbanion leaving group has been proposed.[2]

Another example is the Riehm quinoline synthesis.[3] Here a 1,2-dihydroquinoline intermediate must lose the elements R and H to give the quinoline product. This occurs under the acid conditions of the reaction mixture. If the 1,2-dihydroquinoline is isolated, the aromatization can be carried out in a separate step with acid or base catalysis. Thus, treatment of 2,2,4-trimethyl-1,2-dihydroquinoline (I) with sodium anilide yields 2,4-dimethylquinoline and methane.[4]



This paper reports the results of a study of the acid-catalyzed aromatization of I, one of several unusual reactions of I catalyzed by acid or base.[5,6]

Results

The aromatization of the hydrochloride of I was carried out by heating the pure salt above its melting point or by heating solutions of the hydrochloride of I in appropriate solvents. The hydrochloride of I was relatively soluble in aliphatic polyethers such as diethylene glycol diethyl ether, but the products of reaction in these solvents were complex and obviously involved solvent decomposition. Both diphenylmethane and diphenyl ether dissolved the hydrochloride of I near its melting point and were used as solvents for the aromatization.

Carefully purified hydrochloride of I heated in freshly distilled diphenylmethane or diphenyl ether to 250–260° gave less than 10% reaction after long heating. The gaseous products collected consisted of methane, hydrochloric acid, and, in the case of diphenyl ether, ethane. When 25 mole % of β-naphthalenethiol was added, the reaction at 250–260° proceeded to 83% completion in 1 hr. Reactions with the thiol at lower temperatures gave lower yields; at 160–170° less than

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(1) This paper was presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

(2) R. C. Elderfield and E. C. McClenachan, *J. Am. Chem. Soc.*, **82**, 1975, 1982 (1960), and earlier papers.

(3) J. Levin and P. Riehm, *Ber.*, **19**, 1394 (1886).

(4) W. E. Vaughan, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 329.

(5) D. Craig, *J. Am. Chem. Soc.*, **60**, 1458 (1938).

(6) H. C. Dunathan and I. W. Elliott, *Tetrahedron*, in press.

TABLE I

Solvent	Temp., °C.	Time, hr.	Catalyst[a]	Reaction, %	Gas evolved (from mass spectra)
Ph_2CH_2	260	1	None	5 ± 2	CH_4, HCl
Ph_2CH_2	260	1	RSH (25%)	83 ± 2	CH_4, HCl
Ph_2CH_2	260	4	RSH (30%)	87 ± 2	CH_4, HCl
Ph_2CH_2	160	1.5	RSH (30%)	0	
Ph_2CH_2	170	4	t-Bu_2O_2 (94%)	50 ± 2	CH_4, HCl
Ph_2O	260	5	None	3 ± 1	CH_4, C_2H_6, HCl
Ph_2O	230	2	RSH (25%)	45 ± 2	CH_4, C_2H_6, HCl
Ph_2O	200	2	RSH (25%)	15 ± 5	Gas not analyzed

[a] Given as mole % of the hydrochloride of I; RSH is β-naphthalenethiol.

5% reaction occurred. However, the reaction proceeded to 50% completion when 94 mole % of di-*t*-butyl peroxide was added at 170°.[7] All reactions in diphenylmethane and diphenyl ether were particularly clean; I and VI were the only detectable quinoline products. The results of reactions in solution are given in Table I.

The reaction of the pure hydrochloride of I to give aromatized products occurs at temperatures near its melting point. After 30 min. at 210°, 20% reaction had occurred, while 4 hr. at 230° or 10–15 min. at 289° gave complete reaction. The products of these reactions were quite complex and posed a considerable problem in separation. It was found that v.p.c. on a polyester column afforded separation of the quinoline products into seven fractions. Two of these fractions contained at least two different quinolines making a total of at least nine different quinoline products. Since most of these products are formed in 2 to 12% yield and cannot be separated on preparative scale v.p.c. columns, there has been some difficulty in establishing their identity. Nonetheless, six of these nine have been positively identified; two have been assigned structures on the basis of analytical and spectral data; and the ninth, present in very small quantities, has been assigned a tentative structure.

The components of fractions 1, 2, and 3 are all tetrahydroquinolines as shown by their ultraviolet absorption spectra. Their molecular weights as determined by mass spectra are, respectively, 175, 189 and 189, all ± 4. The first fraction component was identified as 3,4-dihydro-I (2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline) by comparison of its infrared, n.m.r., and mass spectrum with those of an authentic sample of 3,4-dihydro-I and by determining the melting and mixture melting point of the two hydrochlorides.

The molecular weight of the second fraction component indicates a monomethylated dihydro-I. The infrared and n.m.r. spectrum both indicate that the methyl group is on the hetero ring rather than on the benzene ring. The n.m.r. spectrum further shows that the new methyl group has been added to the C-4 methyl group. The resulting ethyl group is seen in a triplet, 9.09 τ (J = 7.5 c.p.s.) at high field and as part of a complex multiplet centered near 8.0 τ. The second fraction component is thus assigned structure III.

The component of fraction 3 was assigned structure IV on the basis of its molecular weight, ultraviolet absorption, infrared absorption at 750 cm.$^{-1}$, and its n.m.r. spectrum (see Experimental section).

The component of fraction 4, present to the extent of only 2%, was thought to be 2,4,8-trimethylquinoline from its infrared and ultraviolet spectra. Synthesis of 2,4,8-trimethylquinoline confirmed this structure (V).

The component of fraction 5 accounted for about 50% of the quinoline product and was readily identified as 2,4-dimethylquinoline (VI).

Fraction 6 consisted of two components. The principal component was shown to be 2,4,7-trimethylquinoline by comparison of its spectrum and its purified picrate with those of an authentic sample of 2,4,7-trimethylquinoline. The minor component was tentatively assigned structure VIII on the basis of a peak in the mixture mass spectrum at 189 ± 4 and ultraviolet absorption corresponding to a 1,2,3,4-tetrahydroquinoline.

Fraction 7 was also a mixture. In this case the fraction was partially resolved under optimum conditions and two crystalline products were separated. One was easily identified as 2,3,4-trimethylquinoline, a product reported by Craig.[5] The other, also a quinoline, was shown by mass spectra to be a trimethylquinoline. Its infrared spectrum was identical with that of an authentic sample of 2,4,5-trimethylquinoline (X).

The products with their assigned structures are listed in Table II with a per cent yield based on the total quinoline product from the acetone anil (about 20% of the acetone anil is converted to a polymeric material). The methyl groups lost by I in yielding VI are almost completely accounted for in the yield of methane and other methylated products. The hydrogen atoms gained and lost do not balance, suggesting that the polymeric material has supplied hydrogen to form some of the tetrahydroquinolines.

The dihydroquinoline obtained from the condensation of 2 moles of methyl ethyl ketone with aniline has been assigned structure XII,[8] 2,4-diethyl-2-methyl-1,2-dihydroquinoline. A n.m.r. spectrum clearly confirms this assignment and rules out alternate structure XI, 2-ethyl-2,3,4-trimethyl-1,2-dihydroquinoline. Decomposition of the hydrochloride of XII gives as the main quinoline product XIII, formed by loss of ethane. The other possible quinoline product, XIV, is formed with a small amount of XIII when XII is decomposed by refluxing with sodium anilide and aniline. These two products are easily distinguished by their n.m.r. spectra.

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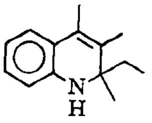
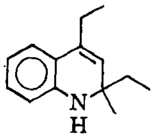
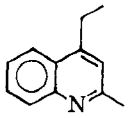
(7) At 170° the half-life for decomposition of t-butyl peroxide is about 1 min. [J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948)]. Thus its direct catalytic action was exerted in only the first few minutes of the reaction.

(8) W. H. Cliffe, *J. Chem. Soc.*, 1327 (1933).


XI


XII


XIII

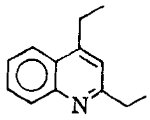
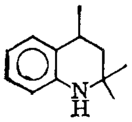
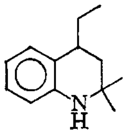
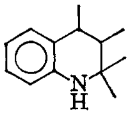
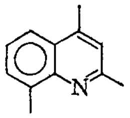
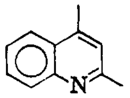
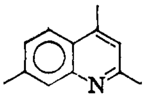
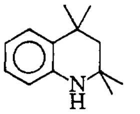
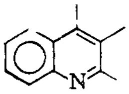
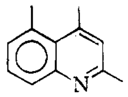

XIV

TABLE II

PRODUCTS OF THE DECOMPOSITION OF 2,2,4-TRIMETHYL-1,2-DIHYDROQUINOLINE HYDROCHLORIDE

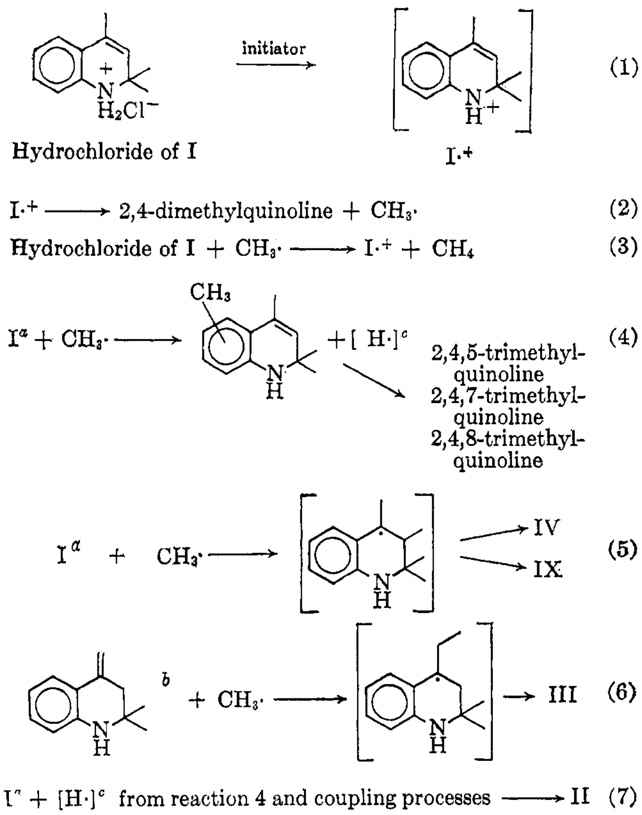
V.p.c. fraction	Structure	Yield, %
1	 II	25
2	 III	12
3	 IV	4
4	 V	3
5	 VI	47
6	 VII  VIII (minor component)	4
7	 IX  X	5
	Methane	24

Discussion

The experimental results clearly indicate a reaction path involving free radicals. Initiation of the reaction by *t*-butyl peroxide and catalysis of the reaction at higher temperatures by β-naphthalenethiol both support this view. β-Naphthalenethiol has been shown to catalyze the transfer of hydrogen between diphenylmethane and diphenylmethyl radicals.[9] The presence of ethane in the gaseous products of decomposition in diphenyl ether is best explained by assuming methyl radical combination.

The products of the reaction without solvent give further evidence for a free-radical mechanism. Isolation of 2,4,5-, 2,4,7-, and 2,4,8-trimethylquinolines is more consistent with the relatively unselective attack of alkyl radicals than with electrophilic substitution by positive methyl species.[10] Formation of products II, III, and IV would be difficult to explain *via* an ionic mechanism but is expected in the presence of methyl radicals and hydrogen atom sources.

SCHEME I



$I\cdot^+ \longrightarrow$ 2,4-dimethylquinoline $+ CH_3\cdot$ (2)

Hydrochloride of I $+ CH_3\cdot \longrightarrow I\cdot^+ + CH_4$ (3)

$I^a + [H\cdot]^c$ from reaction 4 and coupling processes $\longrightarrow$ II (7)

[a] The species undergoing substitution or addition may be hydrochloride of I or I. [b] This double bond isomer of I is formed when I is treated with acid (see ref. 5). [c] Free hydrogen atoms need not be present; the intermediate in the substitution reaction 4 may act as a hydrogen donor.

The reaction scheme shown in Scheme I is in accord with the experimental facts and with the known chemistry of radical species. The first three steps constitute a radical chain reaction. The length of the chain is probably short due to coupling processes. In diphenylmethane the diphenylmethyl radical in all probability acts as a chain carrier.[11] Steps 4 to 7 represent side reactions leading to the observed substitution products.

Results with the aromatization of the diethyl homolog of I, 2,4-diethyl-2-methyl-1,2-dihydroquinoline (XII), are consistent with a radical elimination in that the ethyl group is lost in preference to the methyl.[12]

It is not immediately clear from the scheme in Table II why the acid salt of I is necessary for the loss of methane to occur. The explanation might be found in one of these two possibilities: that the neutral species I is so reactive toward substitution by chain carriers that

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[9] S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 4435 (1955).

[10] 2,4,6-Trimethylquinoline was synthesized and found to have a retention volume very close to that of 2,4-dimethylquinoline under the conditions of the separation. It is quite likely that small quantities of this isomer were present but undetected in the large 2,4-dimethylquinoline peak.

[11] In a single experiment, N,N-dideuterio-2,2,4-trimethyl-1,2-dihydroquinolinium chloride was heated with β-naphthalenethiol in diphenylmethane. The resulting methane contained less than 5% monodeuteriomethane.

[12] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 472.

the chain reaction is stopped, or that production of a neutral "quinolino" radical from I is a higher energy process than production of a "quinolinium" radical from the hydrochloride of I. The second possibility may be supported by reference to recent results of Porter obtained in the flash photolysis of aniline.[13] He has shown that the neutral anilino radical, $C_6H_5NH\cdot$, is a considerably stronger base than aniline itself (pK_a 7.0 *vs.* pK_a 4.6). An enhanced basicity would result if the unshared pair on nitrogen occupied a nitrogen orbital orthogonal to the aromatic π-system. The anilino radical might then have the base strength of a benzoquinuclidine (pK_a 7.8). In this configuration the unpaired spin would be part of a 7-π-electron system which should have electronic transitions similar to those of the benzyl radical. The spectra of the two species are in fact closely similar.[13]

The stability of this configuration suggests that hydrogen atom abstraction from an N–H bond lying perpendicular to the benzene ring leading directly to the seven electron π-system should be easier than abstraction from a bond in the plane of the ring. The neutral species I contains only a single N–H bond which is in or near the plane of the benzene ring. However, in the hydrochloride of I one of the N–H bonds lies nearly perpendicular to the benzene ring. Thus the possibility exists that one role of the proton in the aromatization is to provide an N–H bond with the proper geometric relationship to the adjacent benzene ring.

Experimental

2,2,4-Trimethyl-1,2-dihydroquinoline (I) was prepared by the method of Craig.[5] The hydrochloride was precipitated from an ethanol solution of the reactants and recrystallized from 3 *N* hydrochloric acid, m.p. 208–216°, lit.[5] m.p. 214–216°.

Decomposition of 2,2,4-Trimethyl-1,2-dihydroquinoline Hydrochloride.—The decompositions in diphenylmethane were carried out for the most part on a vacuum line. The solvent was distilled under high vacuum into the flask containing the hydrochloride of I. After heating, the flask was cooled, the gas volume measured, and a sample collected with a Toeppler pump. By isolating the flask in the vacuum line it was possible to heat it to near the boiling point of diphenylmethane. The flask contents were extracted with dilute acid and these extracts neutralized and extracted with ether. The quinolines in the ether solution were analyzed on the v.p.c. column described below. In certain cases the reaction was run under nitrogen rather than high vacuum; this did not affect the extent of reaction.

The decompositions in diphenyl ether were carried out as described for diphenylmethane save that the purified (heat with sodium, distil) solvent was pipeted into the reaction flask.

The results of typical experiments are listed in Table I.

Decomposition of the Hydrochloride of I without Solvent.—These decompositions were carried to completion at temperatures of 270–280° under a slow stream of nitrogen. However, reactions carried out in evacuated and sealed tubes or at lower temperatures gave the same products in essentially the same yields. Gas samples collected from the sealed tube reactions showed the presence of methane and hydrogen chloride but no ethane. The gases were determined by mass spectral analysis. The products were taken up in dilute acid, the extracts neutralized, and the quinolines taken up in ether. A variable amount of polymeric material (10–20%) did not dissolve in the dilute acid. The quinolines from the ether solution were analyzed on a v.p.c. column packed with 10% ethylene glycol isophthalate on Ana-Krome ABS 80–90-mesh support. At 200° the quinolines showed retention times of from 5 to 20 min. at flow rates of 60 ml./min. through a 6-ft. column. At 200° the liquid phase of the column reacted slowly with the quinoline mixture. After a considerable quantity of quinoline mixtures had been passed through the column, this reaction and the consequent bleeding of the column stopped. The column that resulted was of dubious composition but was very effective in this separation. Injection of known mixtures of mixture components showed that the thermal conductivity detector was equally sensitive to the different quinolines within the error of area integration. Samples of a few milligrams were collected in small bore glass tubing and purified by reinjection. All spectra were determined using these samples and in some cases the compounds could be crystallized and recrystallized in the tubes.

Fractions 1, 2, and 3 all showed ultraviolet maxima at 212, 248, and 300 mμ, typical of 1,2,3,4-tetrahydroquinolines. Fraction 1 solidified in the collection tube and was shown to be identical with dihydro-I (II) by comparison of spectra and mixture melting point with the hydrochloride of an authentic sample of II.[14]

Anal. Calcd. for $C_{12}H_{17}N$: C, 82.29; H, 9.71; N, 8.00. Found: C, 82.31; H, 10.01; N, 7.62.

The mass spectrum of fraction 2 showed a parent peak at 189 ± 4 ($C_{13}H_{19}N$) corresponding to a methyl-substituted II. The infrared absorption at 750 cm.$^{-1}$ indicates that the additional methyl group is in the hetero ring rather than on the benzene ring. The n.m.r. spectrum of fraction 2 is consistent with structure III but not with IV or any other isomer. In III the single benzylic hydrogen is coupled with four hydrogens with three different coupling constants and appears as a complex multiplet centered at 7.30 τ. The corresponding multiplet in the spectrum of II appears at 7.2 τ. The four methylene protons of structure III appear in a complex pattern between 7.6 and 8.7 τ with an area integral corresponding to four protons. Of the three methyl groups in III, the geminal pair gives rise to single resonances at 8.90 and 8.81 τ and the third, part of the ethyl group at C-4, appears as a triplet at 9.09 τ (J = 7.5 c.p.s.). The NH proton signal at 6.75 τ and the aromatic multiplet at 3.0 to 4.0 τ complete the spectrum.

The mass spectrum of fraction 3 showed a small peak at 203 ± 4 mass units which was assumed to be due to an impurity. That the much stronger peak at 189 ± 4 represented the true molecular weight was shown by an integral of the compound's n.m.r. peak areas. This showed the ratio of aromatic to all other protons to be 4 to 14.9, confirming the formula $C_{13}H_{19}N$. Fraction 3, isomeric with fraction 2, was assigned structure IV consistent with its n.m.r. spectrum. Single methyl resonances appeared at 9.02 and 8.83 τ while methyl doublets were centered at 9.0 and 8.71 τ (J = 7.0 c.p.s.) in each case. These are assigned to the *gem*-dimethyl group at C-2 and the single methyl groups at C-3 and C-4, respectively. A single proton multiplet centered at 7.65 τ is assigned to the benzylic hydrogen at C-4 and a weak multiplet near 8.4 τ to the tertiary hydrogen at C-3. The NH resonance occurs at 6.73 τ and the aromatic multiplet between 2.9 and 3.8 τ.

Fraction 4, identified as 2,4,8-trimethylquinoline, crystallized in the collection tube, m.p. 41.3–42.5°, lit.[15] m.p. 42°. Its infrared spectrum was identical with that of an authentic sample of 2,4,8-trimethylquinoline, and the melting point of a picrate, 191.8–194.0°, lit.[15] 193°, was undepressed on admixture with 2,4,8-trimethylquinoline picrate.

Fraction 5 was readily identified as 2,4-dimethylquinoline by comparison of its infrared spectrum with that of an authentic sample.[4]

Fraction 6 shows mass peaks starting at mass 187 ± 4 corresponding to a tetramethylquinoline. The n.m.r. spectrum of the mixture shows that most of the methyl groups are attached to unsaturated carbons, the resonances occurring at 7.3 to 7.6 τ. A doublet (J = 7 c.p.s.) occurs at 8.68 τ and a single broad resonance at 3.2 τ. A weak NH resonance is seen at 4.5 τ. The ultraviolet spectrum shows long wave-length maxima at 319, 314, and 306 mμ. The n.m.r. and ultraviolet spectra indicate that the main component is a quinoline unsubstituted at the 3-position (the n.m.r. resonance at 3.2 τ is associated with this hydrogen at C-3 in a number of 2,4-disubstituted quinolines). The major constituent of fraction 6 was identified by comparing the infrared spectrum of fraction 6 with that of an authentic sample of 2,4,7-trimethylquinoline.[16] The melting point of a purified picrate of fraction 6, 227.3–230.0°, lit.[17] 232°, was not depressed on admixture with a picrate of the synthetic material.

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(13) E. J. Land and G. Porter, *Trans. Faraday Soc.*, in press.

(14) I. W. Elliott and P. Yates, *J. Org. Chem.*, **26**, 1287 (1961).

(15) S. Yamaguchi, *J. Pharm. Soc. Japan*, **503**, 4136 (1924).

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Fraction 7 was successfully crystallized in the collection tube, leading to one crop of crystals, m.p. 90–93.5°, easily shown to be identical with an authentic sample of 2,3,4-trimethylquinoline, lit.[5] m.p. 90–92°, by the identity of their infrared spectra. A second crop, m.p. 67–75°, isolated in very small yield, was shown by mass spectra (parent peak at mass 171 ± 4) and ultraviolet spectra (long wave-length maxima at 320, 314, and 307 mμ) to be a trimethylquinoline. The infrared spectrum showed that substitution had occurred in the benzene ring (absorption at 775 and 820 cm.$^{-1}$) and in fact the spectrum proved to be identical with that of an authentic sample of 2,4,5-trimethylquinoline.[16]

"Butanone Anil" 2,4-Diethyl-2-methyl-1,2-dihydroquinoline.—Aniline and 2-butanone reacted according to the procedure given by Vaughan[4] for the preparation of 2,2,4-trimethyl-1,2-dihydroquinoline. 2-Butanone (835 g.) was passed into the reaction mixture of aniline (279 g.) and iodine, (9 g.), which was maintained at 170–175°. The product was crudely distilled to separate butanone and the bulk of the aniline, then fractionated on a 4-ft. glass helix column and the fraction, b.p. 170–174° (28 mm.), 95 g. (lit.[18] b.p. 152–153° at 12 mm.), collected. The n.m.r. showed a vinyl resonance at 4.95 τ, the NH resonance at 6.73 τ, and a quartet centered at 7.55 τ (J = 7.5 c.p.s.), assigned to the methylene group at position 4 of XII. The remainder of the spectrum consisted of the usual aromatic multiplet, a single resonance at 8.82 τ assigned to the methylene group at C-2 of XII, and a pattern of seven lines interpreted as a triplet centered at 8.87τ (J = 7.5 c.p.s.) overlapped on the low field side by a quartet centered at 8.69 τ (J = 7.5 c.p.s.) and on the high field side by a triplet centered at 9.13 τ (J = 7.5 c.p.s.). The seven line pattern thus represents the two methyl groups attached to methylenes at C-2 and C-4, and the methylene attached to the saturated center at C-2.

A sample purified by v.p.c. gave the following analysis.

Anal. Calcd. for $C_{14}H_{19}N$: C, 83.54; H, 9.49. Found: C, 83.53, 83.43; H, 9.17, 9.04.

The hydrochloride of XII, heated for 5 min. at 285°, gave a mixture of quinolines which was analyzed on the previously described v.p.c. column. Six peaks were resolved, one representing *ca.* 50% of the quinoline product. N.m.r. analysis of this peak showed it to be 2-methyl-4-ethylquinoline. (The single methyl resonance occurs at 7.38 τ while the ethyl group gives a quartet at 7.03 τ and a triplet at 8.67 τ).

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.16; H, 7.65; Found: C, 84.23, 84.12; H, 7.75, 7.62.

Base-Catalyzed Decomposition of XII.—The procedure of Vaughan[4] was used on a $^1/_{10}$ scale. XII (0.2 mole, 40.4 g.) refluxed with sodium anilide for 3 hr. V.p.c. analysis of the products showed one major (more than 90%) component. N.m.r. analysis of the product confirmed its structure as 2,4-diethylquinoline. (A triplet representing the six methyl hydrogens falls at 8.63 τ while the two methylene quartets at 7.13 and 7.02 τ overlap to give a five-line pattern.)

Anal. Calcd. for $C_{13}H_{15}N$: C, 84.28; H, 8.16. Found: C, 84.51, 84.27; H, 8.15, 8.20.

2,4,8-Trimethylquinoline (V).—"Acetone *o*-toluidyl," 2,2,4,8-tetramethyl-1,2-dihydroquinoline was prepared by the method of Vaughan[4] for "acetone anil." *o*-Toluidine (1.5 moles, 170 g.) and acetone (500 ml.) yielded 33 g., b.p. 149–154° (30 mm.), lit.[18] b.p. 138.5–139.5° (14 mm.).

Anal. Calcd. for $C_{13}H_{17}N$: C, 83.36; H, 9.16. Found: C, 83.45, 83.29; H, 9.22, 9.04.

"Acetone *o*-toluidyl" (20 g.) was added to the mixture obtained by heating sodium (0.25 g.), *o*-toluidine (3.4 g.), and 0.5 g. of copper powder. The mixture was refluxed for 5 hr., then fractionated with a small Vigreux column, yielding a fraction of 3.46 g. of crude quinoline. Refractionation yielded crystalline V, b.p. 112–114° (3.0 mm.), m.p. 38.7–41.3°, lit.[15] m.p. 42°.

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The Chemistry of Thioether-Substituted Hydroquinones and Quinones. I. The 1,4-Addition of a Heterocyclic Mercaptan to Quinones

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Cyclopentadiene, 1,3-cyclohexadiene, and 2,3-dimethylbutadiene have undergone Diels–Alder addition to a variety of *p*-benzoquinones. The adducts were rearranged to the hydroquinone derivatives and then oxidized to their respective quinones. These quinones undergo normal 1,4-addition of a mercaptan. A new method of rearrangement of the quinone–cyclopentadiene adducts to their hydroquinone forms with triethylamine is reported. The 1,4-addition of a mercaptan to several *o*- and *p*-benzoquinones also is reported.

Many examples of 1,4-additions to quinones are in the literature which include the Thiele acylation reaction,[2,3] the addition of hydrogen halides,[4] of amines,[5] and mercaptans.[6]

The present paper concerns the addition of a heterocyclic mercaptan to unsubstituted, di-, and trisubstituted 1,4-quinones. The succeeding paper[7] concerns the mercaptan addition to monosubstituted 1,4-quinones.

The mercaptan used in this investigation was 1-phenyl-5-mercaptotetrazole[8] (hereafter called HPMT, **1**). The substance is an odorless, high-melting solid which is very acidic, a desirable property in ionic addition reactions to unsaturated compounds.[9] The mechanism of this 1,4-addition is unknown, but whether initial attack is by hydrogen ion, mercaptide ion, or the nucleophilic sulfur atom, the predicted products are the same. Steric effects may influence the course and rate of this reaction.

Addition reactions employing unsubstituted, disubstituted, or trisubstituted quinones normally give good yields of a single product. Contrary to previous reports,[5,9,10] no difficulty was encountered in controlling the reaction in order to obtain the monoaddition product with this mercaptan.

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