The infrared spectrum of a 0.06 M solution in carbon tetrachloride showed absorption bands at 3616 (strong, sharp), 3050 (weak, sharp), and 1645 cm.$^{-1}$ (very weak).

4-*t*-Butyl-1-phenyl-3-cyclohexenol (III).—To 1.20 g. (0.0494 g.-atom) of magnesium turnings in 40 ml. of dry ether was added dropwise with stirring a solution of 13.2 g. (0.0840 mole) of bromobenzene in 30 ml. of dry ether. The mixture was stirred for 1 hr. A solution of 5.00 g. (0.0329 mole) of 4-*t*-butyl-3-cyclohexenone in 25 ml. of dry ether was added dropwise with stirring during 45 min. at 0°. After 1 hr. of continued stirring at 0°, the reaction mixture was poured into ice–water, saturated ammonium chloride solution was added, and the layers were separated. The water layer was extracted with ether. The combined ether layers were washed until neutral with water, dried over anhydrous sodium sulfate, and the ether was removed under reduced pressure. Volatile components of the resulting oil were removed at 25° (0.03 mm.), leaving a solid residue. Two crystallizations from nitromethane gave 0.64 g. (8%) of white crystals, m.p. 74–74.5°. Further recrystallizations from nitromethane yielded a sample for analysis, m.p. 77.5–78.5°.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.42; H, 9.63. Found: C, 83.17; H, 9.69.

The infrared spectrum of a 0.005 M solution[12] showed absorption bands at 3604, 3090, 3062, and 3030 cm.$^{-1}$.

4-*t*-Butyl-1-methyl-3-cyclohexenol (IV).—A solution of 5.00 g. (0.0329 mole) of 4-*t*-butyl-3-cyclohexenone in 25 ml. of anhydrous ether was added to the Grignard reagent prepared from 1.20 g. (0.0494 g.-atom) of magnesium turnings and 11.8 g. (0.0833 mole) of iodomethane in 50 ml. of anhydrous ether. The reaction was carried out as previously described.

The final dried ether solution was concentrated under reduced pressure. The solid residue, m.p. 65°, readily sublimed at 20 mm. Four resublimations yielded white needle-like crystals, 1.0 g. (18%), m.p. 75–75.5°, which showed infrared absorption peaks at 3607 and 3052 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.15; H, 11.90.

Reaction of *p*-*t*-Butylphenol with Lithium in Ethylenediamine. Run 1.—The reported procedure was followed.[4,5] To 7.76 g. (0.0517 mole) of *p*-*t*-butylphenol in 200 ml. of ethylenediamine, was added 2.80 g. (0.40 g.-atom) of lithium metal wire during 2 hr. at 90–100° (nitrogen atmosphere). The mixture was heated at reflux 2 hr. longer. Ultraviolet analysis of the product isolated by ether extraction was consistent with presence of 84% *p*-*t*-butylphenol.

Run 2.—The reaction as in run 1 was repeated with 3.88 g. (0.0259 mole) of *p*-*t*-butylphenol in 200 ml. of ethylenediamine and 8.4 g. (1.20 g.-atom) of lithium. The product contained some *p*-*t*-butylphenol (16% by ultraviolet analysis) and about 20% unconjugated ketones (infrared analysis at 1720 cm.$^{-1}$). The infrared spectrum did not show a detectable absorption band at *ca.* 1340 cm.$^{-1}$.

Acknowledgment.—We wish to thank the National Science Foundation for support of this work.

Aza-Aromatic Substitution. III. Spectral Studies on the Nature of Bromine Complexes with the Quinoline System[1a,b]

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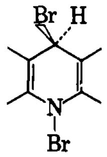
Spectral studies of bromine complexes of quinoline derivatives, both as solid complexes and as solution species, were undertaken. By consideration of the infrared spectrum, ultraviolet spectrum, and solution combining ratios and stability constants it is concluded that the principal species present is a 1:1 quinoline–bromine molecular complex of the n-donor type IV. Re-evaluation of previous reports on purported quinoline–bromine complexes reveals that such isolated compounds were undoubtedly quinolinium perbromides. The relevance of complexes, such as IV, as catalysts in aromatic and aza-aromatic bromination is suggested.

The recently observed facility with which quinoline undergoes selective bromination in the pyridinoid ring[1b] contravenes previous views concerning the reactivity of aza-aromatic heterocycles.[3] The interaction of quinoline and bromine in carbon tetrachloride led to the formation of an intermediate complex I which underwent smooth decomposition at 80° to yield 3-bromoquinoline. Isolation of the novel orange adduct I and iodometric analysis showed it to be an equimolar quinoline–bromine complex.[1b] Although similar halogen addition compounds of aza-aromatic heterocycles and their hydrogen halide salts have been known for some time,[4] the possible role of such adducts in electrophilic aromatic and aza-aromatic substitution makes further information concerning their structure and electronic character most desirable. Thus, the catalytic role of pyridine in aromatic bromination has been ascribed to the intermediate N-bromopyridinium bromide serving as a source of bromine cations.[5] Similar considerations tend to implicate quinoline–bromine adducts in the bromination of quinoline itself.[1]



II

However, the structure of such 1:1 adducts, especially with polynuclear nitrogen heterocycles, has been the subject of some disagreement. The older view of such adducts as being 1,2- or 1,4- addition products of the aza-aromatic heterocycle II[6] has little physical evidence to recommend it as such,[5] although similar structures are often postulated in rationalizing certain aspects of pyridine chemistry.[7] A second structural possibility for such complexes is dicoordinate complexation of the type $(R_3N)_2Br^+Br_3^-$ (III). That perchlorates of

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(1) Previous papers in this series: (a) J. J. Eisch, *J. Org. Chem.*, **27**, 4682 (1962); (b) **27**, 1318 (1962). (c) To whom inquires should be addressed at the Department of Chemistry, Catholic University of America, Washington 17, D.C.

(2) *Cf.* H. S. Mosher in "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 402.

(3) G. M. Badger, "Chemistry of Heterocyclic Compounds," Academic Press, New York, N. Y., 1961, p. 311.

(4) *Cf.* (a) H. Maier-Bode and J. Altpeter, "Das Pyridin und seine Derivate," W. Knapp, Halle, Germany, 1934, pp. 78–79; (b) A. B. Prescott and P. F. Trowbridge, *J. Am. Chem. Soc.*, **17**, 859 (1895); (c) P. F. Trowbridge, *ibid.*, **21**, 66 (1899); (d) D. M. Williams, *J. Chem. Soc.*, 2783 (1931); (e) A. I. Popov, *et al.*, *J. Am. Chem. Soc.*, **79**, 570, 4622 (1957).

(5) R. M. Acheson, T. G. Hoult, and K. A. Barnard, *J. Chem. Soc.*, 4142 (1954).

(6) A. Senier and P. C. Austin, *ibid.*, 1196 (1904).

(7) *Cf.* E. E. Garcia, C. V. Greco, and I. M. Hunsberger, *J. Am. Chem. Soc.*, **82**, 4430 (1960).

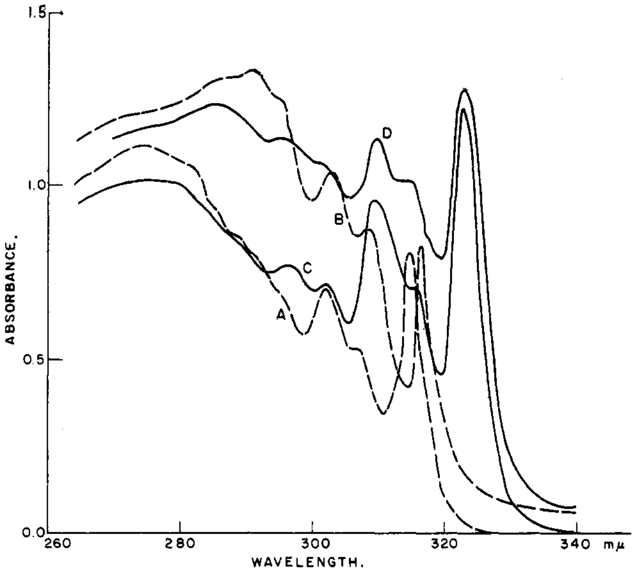

Fig. 1.—Ultraviolet spectra in CCl_4: A, quinoline (2.77×10^{-4} M); B, quinoline (2.77×10^{-4} M) and bromine (2.51×10^{-3} M); C, 3-bromoquinoline (2.77×10^{-4} M); and D, 3-bromoquinoline (2.77×10^{-4} M) and bromine (1.86×10^{-2} M).

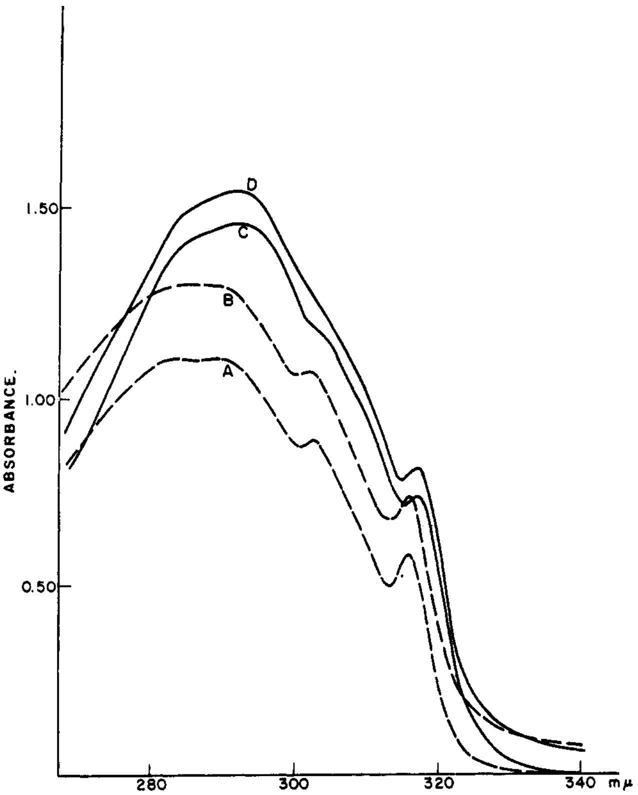

Fig. 2.—Ultraviolet spectra in CCl_4: A, 8-methylquinoline (2.77×10^{-4} M); B, 8-methylquinoline (2.78×10^{-4} M) and bromine (4.5×10^{-2} M); C, 8-bromoquinoline (2.77×10^{-4} M); and D, 8-bromoquinoline (2.78×10^{-4} M) and bromine (1.8×10^{-2} M).

the diquinoline- and diisoquinolinebromine cation actually have been prepared[8] demands that this structure be given serious consideration. The third proposed structure represents these complexes as donor-acceptor complexes of the *n*-donor type. In this structure the unshared electron pair on the nitrogen is involved as the Lewis base center $R_3\overset{\delta+}{N}\rightarrow\overset{\delta-}{Br}\ldots Br$ (IV). Representation of the acridine–bromine adduct as a "bromodinium bromide"[9] would be an extreme ionic example of this type.[5] The fourth viewpoint is that such complexes are really of the π-donor type.[9] This implies the bonding occurs by a charge-transfer process involving the π-electrons of heterocycle V.

In the present investigation the stoichiometry and spectral properties of quinoline–bromine adducts formed both as isolable complexes and as solution species in carbon tetrachloride were examined. Furthermore, to gain insight into the structure of such halogen complexes in solution, the stability constants K_c of bromine adducts with quinoline itself and with suitably substituted quinolines were determined.

Results

Although a 1:1 adduct of quinoline and bromine was described by Lubavin,[10] the reported mode of preparation strongly discredits any claim of success. In fact, the method employed (the action of bromine on quinoline hydrobromide) is actually a most suitable method for the preparation of $C_9H_7NHBr{\cdot}Br_2$, quinolinium tribromide (VI).[11] As reported previously, the successful isolation of a genuine 1:1 adduct I demands the mixing of the cooled components in dry, aprotic solvents in the absence of light.[1b]

Similarly, the description of a 1:2 adduct of quinoline and bromine by Grimaux[12] also can be viewed with skepticism. Admixture of quinoline with an excess of bromine in aqueous suspension and subsequent recrystallization of the red solid from hot chloroform did not seem to preclude the possibility of hydrogen bromide generation and hence the formation of quinoline hydrobromide perbromides. Repetition of Grimaux's work in an aprotic solvent without heating yielded a product VII qualitatively similar to that reported previously.[12] However, iodometric analysis gave "available" bromine values in excellent agreement with a composition $C_9H_7NHBr{\cdot}Br_4$. Reduction of the complex with sulfurous acid and treatment with alkali formed only pure quinoline, demonstrating that no substituted nucleus was present in the complex. In addition, the infrared spectrum displayed the trio of sharp intense bands at 1560, 1600, and 1640 cm.$^{-1}$, which are a prominent feature in the spectra of authentic quinolinium bromide and quinolinium tribromide themselves. Therefore, it is concluded that Grimaux's "quinoline tetrabromide" is really quinolinium pentabromide (VII),[4c] the hydrogen bromide arising from the facile bromination of part of the quinoline present.[13] The lability of this complex (equation 1) is seen in the fact its ultraviolet spectrum in dilute solution markedly resembles that of quinolinium tribromide, the tribromide absorption at 273 mμ being most prominent.

$$[C_9H_7NH]^+Br_5^- \rightleftarrows [C_9H_7NH]^+Br_3^- + Br_2 \qquad (1)$$

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[8] P. B. D. de la Mare, M. Kiamud-din, and J. H. Ridd, *Chem. Ind.* (London), 727 (1959).

[9] W. Slough and A. R. Ubbelohde, *J. Chem. Soc.*, 911 (1957).

[10] N. N. Lubavin, *Russ. J. Phys.-Chem. Soc.*, **18**, 434 (1886).

[11] A. Claus and F. Collischonn, *Ber.*, **19**, 2763 (1886).

[12] E. Grimaux, *Bull. soc. chim. Paris*, [2] **38**, 124 (1882).

[13] This conclusion does not imply that higher adducts of bromine and quinoline cannot exist in solvent-free systems at lower temperatures (*cf.* ref. 9).

Previous infrared spectral examination of the solid 1:1 quinoline–bromine adduct I had suggested that the quinoline system is not perturbed markedly in the complex.[1b] Certain shifts in the out-of-plane hydrogen deformations in the 950-cm.$^{-1}$ region and in the C=C, C=N ring stretching vibrations in the 1600-cm.$^{-1}$ region resemble those observed in the spectrum of quinoline methiodide itself. The low frequency quinoline band at 1579 cm.$^{-1}$ is shifted to 1595 cm.$^{-1}$ in both I and the methiodide.

The ultraviolet spectrum of quinoline–bromine solutions in carbon tetrachloride measured against pure solvent (Fig. 1, B) shows definite changes over the spectrum of quinoline itself (Fig. 1, A). Notable is the development of a new absorption band at 290 mμ (ϵ 4000 ± 400). In addition, the quinoline peak at 314.5 mμ is shifted to 316.5 mμ in the presence of bromine. That no marked additional absorption is displayed in the 260–280 mμ argues against the presence of any significant amount of the tribromide ion. Similarly, the spectrum of the 3-bromoquinoline–bromine solution (Fig. 1, D) displays a new peak at 284 mμ, as shown by comparison with the spectrum of 3-bromoquinoline itself (Fig. 1, C). On the other hand, no marked shifts in the heterocycle's peaks themselves occur.

Similar spectral comparisons of heterocycle–bromine solutions with the spectra of 8-methylquinoline (Fig. 2, A, B) and of 8-bromoquinoline (Fig. 2, C, D), respectively, reveal no significant change in the absorption bands.

TABLE I

APPARENT STABILITY CONSTANTS OF BROMINE COMPLEXES WITH QUINOLINES IN CARBON TETRACHLORIDE

Compound	Apparent stability constant, K_c, l./moles	Slope, molar ratio	Method	Temp., °C.	Basicity, K_b
Quinoline	113 ± 6	1.0	A[a]	22	4.9×10^{-10}[c]
	118 ± 3	..	B[b]	21	
	115 ± 3	..	B[d]	21	
3-Bromoquinoline	12.7 ± 1.3	1.05	A[a]	20	3.2×10^{-12}[c]
	11.8 ± 0.7	..	B[b]	20	
	12.1 ± 0.7	..	B[d]	20	
8-Bromoquinoline	1.1 ± 0.2	..	B[b]	16	7.5×10^{-12}[c]
8-Methylquinoline	4.8 ± 0.5	..	B[b]	16	3.1×10^{-10}[e]

[a] Method of Kingery and Hume (ref. 23). [b] Method of Benesi and Hildebrand (ref. 24) applied to "difference" absorbance measurements as a function of bromine concentration. [c] Ref. 18. [d] Method of Benesi and Hildebrand (ref. 24) applied to "difference" absorbance measurements as a function of the quinoline concentration. [e] C. Golumbic and M. Orchin, *J. Am. Chem. Soc.*, **72**, 4145 (1950).

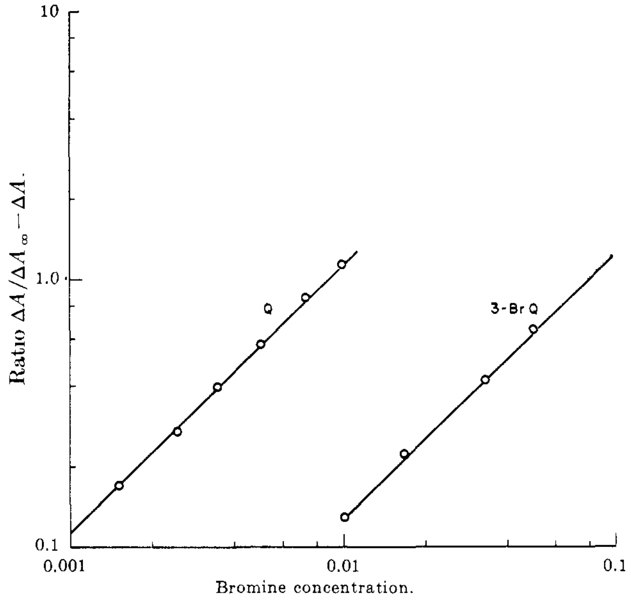


Fig. 3. Logarithmic plot of $\Delta A/\Delta A_\infty - \Delta A$ *vs.* bromine concentration for quinoline (Q) and 3-bromoquinoline (3-BrQ).

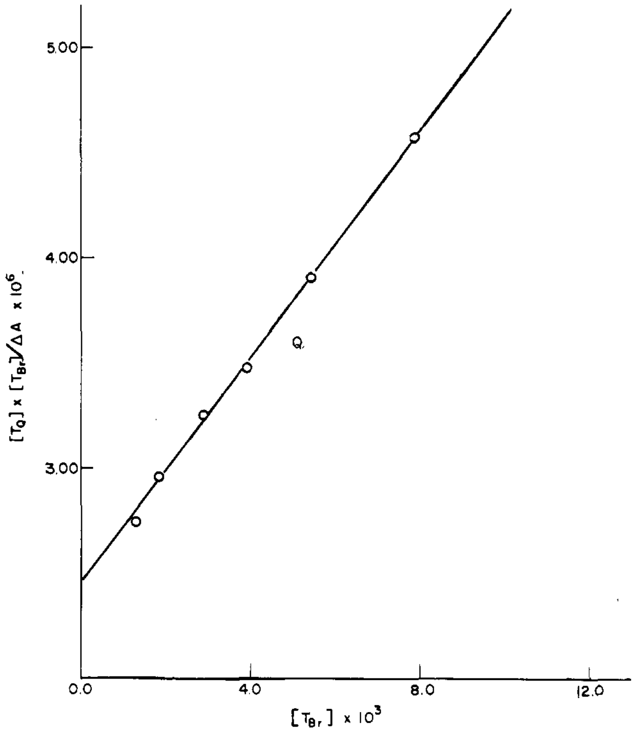


Fig. 4.—Benesi–Hildebrand plot of $[T_Q]$ $[T_{Br_2}]/\Delta A$ *vs.* $[T_{Br_2}]$ for bromine–quinoline complexes.

As described in detail in the Experimental section, the combining ratios for the complex formed from bromine and both quinoline and 3-bromoquinoline, respectively, were determined from the slope in the logarithmic plot of $\Delta A/\Delta A_\infty - \Delta A$ versus the bromine concentration (Fig. 3). The necessary data were drawn from "difference" spectra, which were obtained by recording the absorbance of quinoline–bromine solutions against a quinoline solution standard of the same concentration. Both heterocycles were found to form only 1:1 adducts, even when bromine concentration was increased twenty-fold over that of the heterocycle (equation 2). No significant amount of higher bromine-containing complexes could be detected.

$$R_3N: + Br_2 \rightleftarrows R_3N:Br_2 \qquad (2)$$

The apparent stability constants K_c of the heterocycle–bromine complexes formed (equation 2) were determined from "difference" spectral absorbance data by means of the logarithm ratio method of Kingery and Hume[23] and by the method of Benesi and Hildebrand.[24] Not only were such stability constants determined for quinoline and 3-bromoquinoline, but also for 8-methylquinoline and 8-bromoquinoline (Fig. 4, 5). The resulting values for the stability constants are presented in Table I.

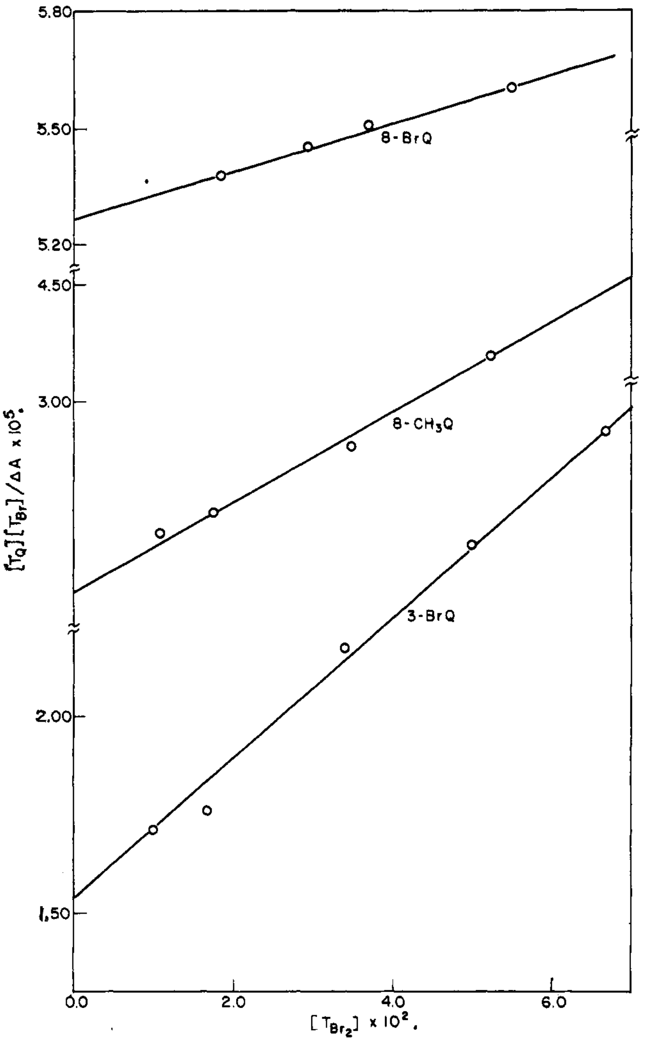
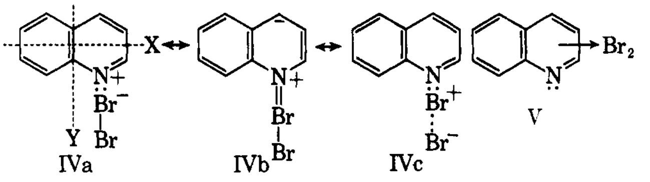


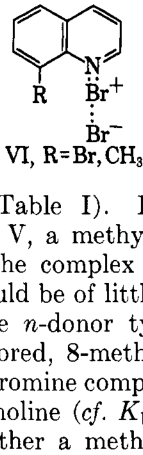
Fig. 5.—Analogous Benesi-Hildebrand plots for bromine complexes of 3-bromoquinoline (3-BrQ), 8-bromoquinoline (8-BrQ), and 8-methylquinoline (8-CH_3Q).

Discussion

In the present study only 1:1 heterocycle-bromine complexes could be detected in solution (equation 2) and a previous report[12] concerning a solid "quinoline tetrabromide" (1:2 adduct) was discredited. Of the various structural models proposed for the equimolar adduct (II-V),[5-9] 1,2- and 1,4-adducts (II) seem the least attractive. In fact, the low solubility of the adduct in various solvents would be inconsistent with the presumedly covalently bonded halogens of structure II. The infrared spectral similarities between the quinoline-bromine adduct I and quinoline methiodide on the one hand, and I and quinoline itself on the other hand, do not favor adducts of type II. Moreover, a detailed study of acridine-bromine complexes involving model compounds of type II reached the same conclusion.[5] As to the view that I may be bromine diquinoline tribromide, $(C_9H_7N)_2Br^+Br_3^-$ (III), the absence of any tribromide ion absorption in the ultraviolet spectrum of quinoline-bromine solutions (Fig. 1, B) eliminates this possibility.

The decision as to which of the remaining two structural models (IV, *n*-donor, or V, *π*-donor) represents the nature of the 1:1 quinoline-bromine adduct I cannot be made without some reservation. The Benesi-Hildebrand method for determining stability constants works equally well if one is dealing with a single type of 1:1 complex or an infinite number of 1:1 complexes.[14] Hence, both types of complexes could exist simultaneously in the quinoline-bromine system. However, two additional considerations favor the *n*-donor type IV as being the predominant complex in this system. First, the magnitudes of the stability constants (Table I) are much more consonant with those encountered with *n*-donors of the oxygen- and nitrogen type,[15] than with *π*-donors of the aromatic type. Thus the stability constant of the bromine complex of naphthalene has a value of 0.23[16] (*vs.* 115 for quinoline). Also the absorption maxima of the complexes are quite divergent (346 mμ[16] *vs.* 290 mμ). Secondly, the effect of substituents on the stability constants of complexes of quinoline derivatives with bromine is more in accord with an *n*-donor type. The decreased stability of the 3-bromoquinoline-bromine adduct is consistent with the lower basicity of this heterocycle toward protons, compared with quinoline itself. More noteworthy is the lowered stability of bromine complexes VI with both 8-bromoquinoline and 8-methylquinoline (Table I). If the complex were of the *π*-donor type V, a methyl group would be expected to enhance the complex stability somewhat.[17] Steric hindrance should be of little importance. If the complex were of the *n*-donor type VI, and if steric factors could be ignored, 8-methylquinoline would be expected to form a bromine complex of comparable stability to that of quinoline (*cf.* K_b in Table I). However, situation of either a methyl group or a bromo group at the 8-position would be expected to block approach of the bromine molecule to the tertiary nitrogen atom in the plane of the heterocyclic ring. Again, the lower stability of these complexes suggests that *n*-donor complexes are the important species present in quinoline-bromine solutions. However, these arguments do not rule out the presence of small, but significant, amounts of *π*-complexed quinoline-bromine molecules. Indeed, as the *n*-donor character of the heterocycle decreases (as with 8-bromoquinoline), *π*-donor character may become more prominent.


IVa IVb IVc V


VI, R=Br, CH_3

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[14] L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957). A temperature independence of total oscillator strength integrated over the charge-transfer band would be a good criterion for a single complex.

[15] *Cf.* H. Tsubomura, *ibid.*, **82**, 40 (1960), for similar considerations in determining the *n*- or *π*-donor character of N,N-dimethylaniline-iodine complexes.

[16] N. W. Blake, H. Winston, and J. A. Patterson, *ibid.*, **73**, 4437 (1951).

[17] L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952), have reported the following K_c values for I_2 and ICl complexes, respectively: benzene, 0.15 and 0.54; toluene, 0.16 and 0.87.

A further point to be considered is the ultraviolet absorption spectrum of the quinoline–bromine complex. In a correlative study of the ultraviolet absorption spectra of naphthalene and quinoline derivatives,[18] the spectral shifts encountered in quinoline's E_2 (276 mμ) and B (313 mμ) bands were found to accord with changes in molecular dimensions.[19] The B band exhibits a red shift with increasing molecular length (X-axis of IVa) and therefore is longitudinally polarized along this axis. On the other hand, the E_2 band undergoes a bathochromic shift with structural changes which increase the molecular width (Y-axis in IVa) and is therefore transversely polarized. Thus, the 3-bromo- and 8-bromoquinolines display their E_2 bands at 279 and 291 mμ, and their B bands at 323 and 315 mμ, respectively.[18] With reference to IVa, an *n*-donor complex would be expected to exhibit a large shift in quinoline's E_2 band (276 → 290 mμ), since the molecular width (Y-projection) has been increased. Since the molecular length (X-projection) has been essentially unchanged, the B band should be affected but little (314.5 → 316.4 mμ in carbon tetrachloride)

In reference to the *n*-donor representation in IV, there exists the formal possibility of back-donation or charge transfer from the bromine to the π-molecular orbitals of the heterocycle IVb. This is reminiscent of electronic descriptions entertained for such systems as pyridine N-oxide.[20] Further studies with other aza-aromatic systems will attempt to assess the importance of such p_π-π effects.

Finally, the partially polarized bromine molecule, approximated by extreme structure IVc, could well serve as a potential source of cationic bromine and, hence, function as a selective electrophilic brominating agent, as previously suggested.[1b,5] Heterolysis of the polarized bromine–bromine bond in such a complex, forming $[R_3N:Br]^+$, Br^-, would be facilitated by ionizing solvents. This may explain the rapid, nonselective bromination of quinoline in polar solvents.[1b]

Experimental

Starting Materials.—The quinoline, 3-bromoquinoline, 8-bromoquinoline, bromine, and carbon tetrachloride were carefully purified and dried as described in a previous paper.[1b] Reagent grade 8-methylquinoline was dried over potassium hydroxide pellets and then fractionally distilled twice through a 1 × 50 cm. heated fractionation column filled with 3 mm. glass helices, b.p. 110–111° (7 mm.). Finally, the quinolines and bromine were fractionally redistilled just before use.

Instrumental Analyses.—The infrared data were obtained on samples as powder films or mineral oil mulls by means of a Perkin-Elmer Model 137 infrared spectrophotometer. The ultraviolet spectra were measured with a Cary Model 11 recording ultraviolet spectrophotometer.

Iodometric Analyses.—Samples of the 1:1 quinoline–molecular bromine complex and the complexes of quinolinium bromide with bromine ($C_9H_7N{\cdot}HBr{\cdot}Br_2$ and $C_9H_7N{\cdot}HBr{\cdot}Br_4$) were prepared and dried in the absence of light.[1b] These complexes were analyzed for available bromine equivalents iodometrically in the usual manner.[1b]

"Quinoline Tetrabromide."[12]—Addition of a dilute solution of quinoline in carbon tetrabromide to a relatively concentrated solution of a sixfold excess of bromine in the same solvent gave, upon further standing at room temperature, a deposit of dark red crystals. The dried product, which lost bromine vapor slowly upon standing, was weighed promptly in a small, capped weighing bottle with little air space. The iodometric analysis gave an equivalent weight more consistent with quinolinium pentabromide,[4c] rather than with Grimaux's postulated "quinoline tetrabromide."[12]

Anal. Calcd. for $C_9H_7N{\cdot}Br_2$: active Br equiv., 144.5. Calcd. for $C_9H_7N{\cdot}Br_4$: active Br equiv., 112.2. Calcd. for $C_9H_7N{\cdot}HBr{\cdot}Br_4$: active Br equiv., 132.5. Found: active Br equiv., 132.

The infrared spectrum of this complex resembled the spectra of authentic quinolinium bromide and quinolinium tribromide, especially in the trio of sharp, intense bands at 1560, 1600, and 1640 cm.$^{-1}$ (this trio occurs at 1575, 1605, and 1625 cm.$^{-1}$ in quinoline itself). The ultraviolet spectrum of the red complex in carbon tetrachloride (with a small amount of *t*-butyl alcohol for solubilization) displayed the usual quinoline bands at 301 and 314.5 mμ. In addition, the pronounced absorption at 273 mμ suggested the tribromide ion.[21] (The other quinoline peak at 276 mμ was no longer discernible.)

Moreover, treatment of an aqueous suspension of the red complex at low temperatures with gaseous sulfur dioxide and work up by base treatment and ether extraction gave the free quinoline. The infrared spectrum of the recovered quinoline contained no bands indicative of substitution on the nucleus.[1b]

Ultraviolet Spectral Determination of Stability Constants of Bromine Complexes with the Quinolines. (A) Preparation and Handling of Solutions.—The standard solutions of the quinolines and of bromine in carbon tetrachloride were prepared by direct weighing of the freshly distilled components (the bromine being weighed into a tared amount of solvent) in stoppered weighing bottles and the subsequent dilution of the samples with fresh solvent. By dilution of appropriate aliquots, the various solutions for spectral measurements were obtained. For reliable results such solutions had to be protected from light and moisture. To this end all solvent was dried scrupulously and the volumetric flasks covered with aluminum foil.

(B) **Measurement of Ultraviolet Spectra.**—The preparation and spectral measurement of the quinoline–bromine solutions in carbon tetrachloride were performed in a darkened room. The quinoline–bromine solutions kept in the dark showed no change in their ultraviolet spectra with time. Exposure to light, especially of the ordinary tungsten filament sort, eventually caused the formation of turbid solutions. Solutions of 8-methylquinoline–bromine were particularly light sensitive.[22]

The ultraviolet spectra of quinoline, 3-bromoquinoline, 8-methylquinoline, and 8-bromoquinoline in carbon tetrachloride measured against a solvent blank are reproduced in Fig. 1, A, C and 2, A, C, respectively. In the range of concentrations employed (10^{-4} to 10^{-3} *M*) these solutions obeyed Beer's law. The ultraviolet spectra of mixtures of bromine with the individual quinolines in carbon tetrachloride measured against a solvent blank are reproduced in Fig. 1, B, D and 2, B, D, respectively. The small absorbance of the molecular bromine in the region of interest was subtracted from the observed spectra.

The ultraviolet "difference" spectra were obtained by measuring the ultraviolet spectra of the bromine–quinoline mixtures against a standard of the quinoline alone of the same initial concentration. Various differential absorption spectra were then obtained by keeping the quinoline concentration constant and varying the bromine concentration. The "difference" spectra were corrected for molecular bromine absorbance. Alternatively, the bromine concentration in the quinoline–bromine mixtures was held constant and the quinoline concentration was varied. In the latter series of measurements, of course, the standard cell always was provided with the quinoline of the proper initial concentration.

(C) **Treatment of Data.**—The combining ratios of quinoline and of 3-bromoquinoline with molecular bromine were determined by measuring the "difference" absorbance, ΔA, as a func-

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(18) S. B. Knight, R. H. Wallick, and J. Bowen, *J. Am. Chem. Soc.*, **76**, 3780 (1954).

(19) (a) G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939); (b) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

(20) E. P. Linton, *J. Am. Chem. Soc.*, **62**, 1945 (1940), reported dipole moment data in accord with back-donation contributions for pyridine-N-oxide.

(21) The tribromide ion is reported to absorb at 275 mμ in ethylene chloride [R. E. Buckles, A. I. Popov, W. F. Zelezny, and R. J. Smith, *ibid.*, **73**, 4525 (1951)] and at 268 mμ in a 9:1 methanol–water mixture [W. A. Bonner, *ibid.*, **74**, 5078 (1952)].

(22) Although ultraviolet spectra of quinoline–bromine complexes could be recorded in freshly purified, reagent chloroform, such solutions were extraordinarily prone to decomposition upon brief exposure to light. Quinolinium bromide and 3-bromoquinoline peaks signaled the onset of such side reactions. *Cf.* ref. 5 for the study of the acridine–bromine complex in chloroform.

tion of the bromine concentration in the wave-length range of 280–340 $m\mu$, where the slit opening remained practically constant and the bromine absorption was relatively low. The "difference" absorbance (corrected for bromine absorbance) was plotted against the increasing bromine concentration until it reached a constant value, ΔA_∞, due to the complex alone. The slope in the logarithmic plot of $\Delta A/\Delta A_\infty - \Delta A$ *vs.* the bromine concentration yields the combining ratios (Fig. 3). The logarithmic ratio extrapolated to the 1.0 *M* bromine concentration affords the apparent stability constant. The foregoing method is described by Kingery and Hume[23] (method A).

Another method employed for determining the apparent stability constants of the quinolines was that described by Benesi and Hildebrand.[24] A comprehensive and critical review of the various methods of calculating stability constants has appeared recently.[25] In the present approach the stability constants were determined from the plot of the following function of the total concentrations, $[T_Q]\cdot[T_{Br_2}]/\Delta A$ *vs.* $[T_{Br_2}]$, where T_Q is the total initial concentration of the quinoline, T_{Br_2} the total initial concentration of the bromine, and ΔA the "difference" absorbance (Fig. 4 and 5). The slope yields the reciprocal of $\Delta\epsilon$, the difference between the molar absorptivities of the resulting complex and the respective quinoline, and the intercept provides the reciprocal of the product, $\Delta\epsilon\cdot K_c$, where K_c is the stability constant (method B).

The apparent stability constants obtained by these methods are summarized in Table I.

By study of the interaction of bromine with carbon tetrachloride in perfluorohydrocarbon solvents, it was shown that any bromine–carbon tetrachloride complexes are much weaker than the quinoline complexes examined. Hence, corrections for this solvent interaction can be neglected.

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[23] W. D. Kingery and D. N. Hume, *J. Am. Chem. Soc.*, **71**, 2393 (1949).

[24] H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

[25] M. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).

Organosilicon Compounds with Functional Groups Proximate to Silicon. II. Lithium Aluminum Hydride Reduction of Epoxyethylsilanes[1]

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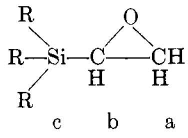
To evaluate the electronic impact of the silicon atom on the mode of behavior of an adjacent epoxide linkage, the lithium aluminum hydride reduction of a series of epoxyethylsilanes was investigated. Whether the R group in  $R_3Si\overset{O}{CH-CH_2}$ (I) was ethyl, benzyl, phenyl, or a *p*-substituted phenyl group, the predominant reduction product was the 2-substituted ethanol. That this primary alcohol arose from the direct hydride ion attack at the carbon alpha to silicon in I was demonstrated by a deuterium tracer study. The electronic factors involved in this novel reduction of epoxyethylsilanes are considered in the light of current theory.

In the previous paper of this series[1] the feasible synthesis of epoxyethylsilanes was reported for the first time. The chemical versatility of these systems offers an excellent opportunity for evaluating the electronic influence of the adjacent silicon atom on the behavior of the epoxide linkage (I). The present study reports results obtained from the lithium aluminum hydride reduction of epoxyethylsilanes (I), where both the electronic nature of R and the experimental conditions were varied. Presumably occurring by the nucleophilic attack of a complexed hydride ion,[3] this reaction offered the possibility of estimating the importance of three modes of attack. Not only could nucleophilic attack be expected at the secondary (Ib) and the primary carbons atoms (Ia) of the epoxide group, but also at the positive-polarized silicon atom (Ic). Indeed, as further research with epoxyethylsilanes has shown, certain nucleophiles, *e.g.*, phenyllithium and amines, effect carbon–silicon bond cleavage as the principal reaction.[4]



I

Results

In order to establish the general character of these epoxide reductions, the behavior of epoxyethyltriphenylsilane toward lithium aluminum hydride in tetrahydrofuran was examined in detail. Although the poor material balances obtained from reductions conducted at 66° indicated the occurrence of much carbon–silicon bond cleavage, reduction at 25° and usual work-up gave an excellent recovery of reduction products. When the epoxide–lithium aluminum hydride ratio was 1.0:3.25, the ratio of secondary to primary alcohols determined by gas chromatography was 1:6.5. Moreover, at an epoxide–lithium aluminum hydride ratio of 1.0:0.75, the primary alcohol was the sole product (Table I). Structures of the alcohols formed in reduction were verified by separating the isomers by column chromatography and comparing them with samples synthesized by unambiguous methods (Chart I). Thus, in contrast to other monosubstituted epoxides,[3] this epoxyethylsilane displays a decided preference for reduction to the primary alcohol, 2-(triphenylsilyl)-ethanol (III).

In assessing the significance of the foregoing, unexpected mode of epoxide reduction, it was desirable to show conclusively that the primary alcohol resulted from attack of the hydride ion at the secondary carbon atom. Since the lithium aluminum hydride reduction of epoxides with[3b] or without[5] Lewis acid additives can

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[1] Paper I in this series: J. J. Eisch and J. T. Trainor, *J. Org. Chem.* **28**, 487 (1963).

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[3] (a) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959); (b) M. N. Rerick and E. L. Eliel, *J. Am. Chem. Soc.*, **84**, 2356 (1962), and references cited therein.

[4] In unpublished studies of this laboratory phenyllithium has been shown to react readily with epoxyethyltriphenylsilane to yield tetraphenylsilane.

[5] H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).