shift, and its position (230 mμ, ε 6,400) even suggests that this partial represents the resonance of only the thiophene ring.[10]

The secondary maximum of 2-(3-methylthienyl) styryl ketone differs from the 4- and 5-methyl analogs in the styryl ketones as much as it does in the methyl ketones, and presumably the hyperconjugation phenomenon suggested for the methyl ketone again is involved.

It is of interest to compare the spectrum of furfural-2-acetothienone with those of benzal-2-acetothienone (2-thienyl styryl ketone) and furfuralacetophenone.[8] The electron donating quality of the 2-furyl group is apparent from the bathochromic shift of the 310 mμ band of chalcone to 344 mμ (ε 26,800) in furfuralacetophenone. This shift of some 34 mμ is almost duplicated when the 2-furyl group replaces the phenyl group of benzal-2-acetothienone to give furfural-2-acetothienone (from 320 to 353 mμ). Similarly, the effect of the replacement of the phenyl by a 2-thienyl group gives an almost constant bathochromic shift of 9–10 mμ in both the furan and benzene series. Thus, the replacement of the phenyl group in chalcone by the 2-thienyl group causes a shift of the maximum from 310 mμ to 320 mμ, while the maximum of furfural acetophenone (344 mμ) is displaced in furfural-2-acetothienone to 353 mμ. The spectrum of furfural-2-acetothienone also exhibits the secondary maximum at 244 mμ typical of the secondary maxima encountered in the 2-thienyl styryl ketones.

Acknowledgment.—We wish to thank the Socony–Vacuum Oil Co. for the generous gift of a number of thiophene chemicals, and the Research Corporation for defraying a portion of the cost of this project.

PITTSBURGH, PENNA. RECEIVED DECEMBER 7, 1950

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[10] The maxima of thiophene and alkyl thiophenes are reported in the 231–237 mμ range (Appleby, *et al.*, THIS JOURNAL, **70**, 1552 (1948); Kuhn and Dann, *Ann.*, **547**, 293 (1941); also ref. (5)).

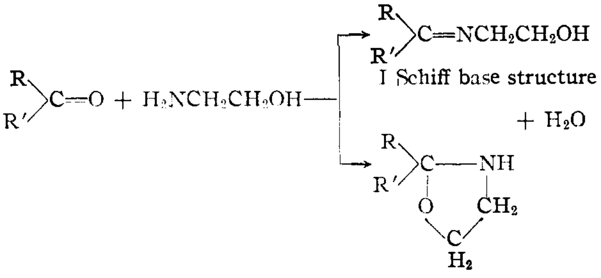
[CONTRIBUTION OF THE NAVAL RESEARCH LABORATORY]

Infrared Spectra and Structure of Reaction Products of Ketones and Ethanolamine[1]

BY L. W. DAASCH

The structure of products obtained in the condensation of aliphatic ketones with ethanolamine can be postulated to be either a Schiff base or an oxazolidine ring. The infrared spectra presented for some of these products indicates the Schiff base structure forms in preference to the oxazolidine ring structure. In certain instances this is contradictory to the structures reported on the basis of other physical properties.

The infrared spectra of the reaction products of certain aromatic aldehydes and ethanolamine have indicated that the structure in these cases was a Schiff base[2] rather than an oxazolidine.[3] It was of interest to extend the investigation to products prepared from aliphatic ketones and ethanolamine where the reaction could also lead either to a Schiff base (I) or an oxazolidine ring structure (II). The choice between these structures has previously been made on the basis of the compound's viscosity, refractive index, solubility in water, and on the difference in boiling points of the compound and its reduction product. By correlating these physical properties some of the compounds investigated here have been given structure (I) and others structure (II).[4] The structure of four ketone-ethanolamine condensation products has been determined through a study of their infrared spectra.



II Oxazolidine structure

Discussion

The infrared spectrum of compounds with structure (I) may be expected to show absorption around 1650 cm.$^{-1}$ due to the C=N bond while structure (II) should have no corresponding absorption.[2] Both structures should produce absorption bands around 3300 and 1150 cm.$^{-1}$ due to OH (bonded) and C–OH linkages, respectively, in structure (I), and due to NH (bonded) and C–O–C, respectively, in structure (II).[5] By obtaining the spectrum of dilute solutions in non-polar solvents one can frequently determine whether the 3300 cm.$^{-1}$ band is an OH or NH absorption and this provides another spectral difference between structures (I) and (II). In the present instance solution work was unnecessary since the C=N correlation reliably distinguishes between structures (I) and (II).

The spectra of compounds prepared from the reactions of methyl *n*-propyl ketone, diisobutyl ketone, methyl *n*-amyl ketone, and cyclohexanone with ethanolamine are shown in Figs. 1, 2, 3 and 5. Figures 4 and 6 are, respectively, the spectra of the compounds prepared from methyl *n*-amyl ketone and cyclohexanone with the secondary amine,

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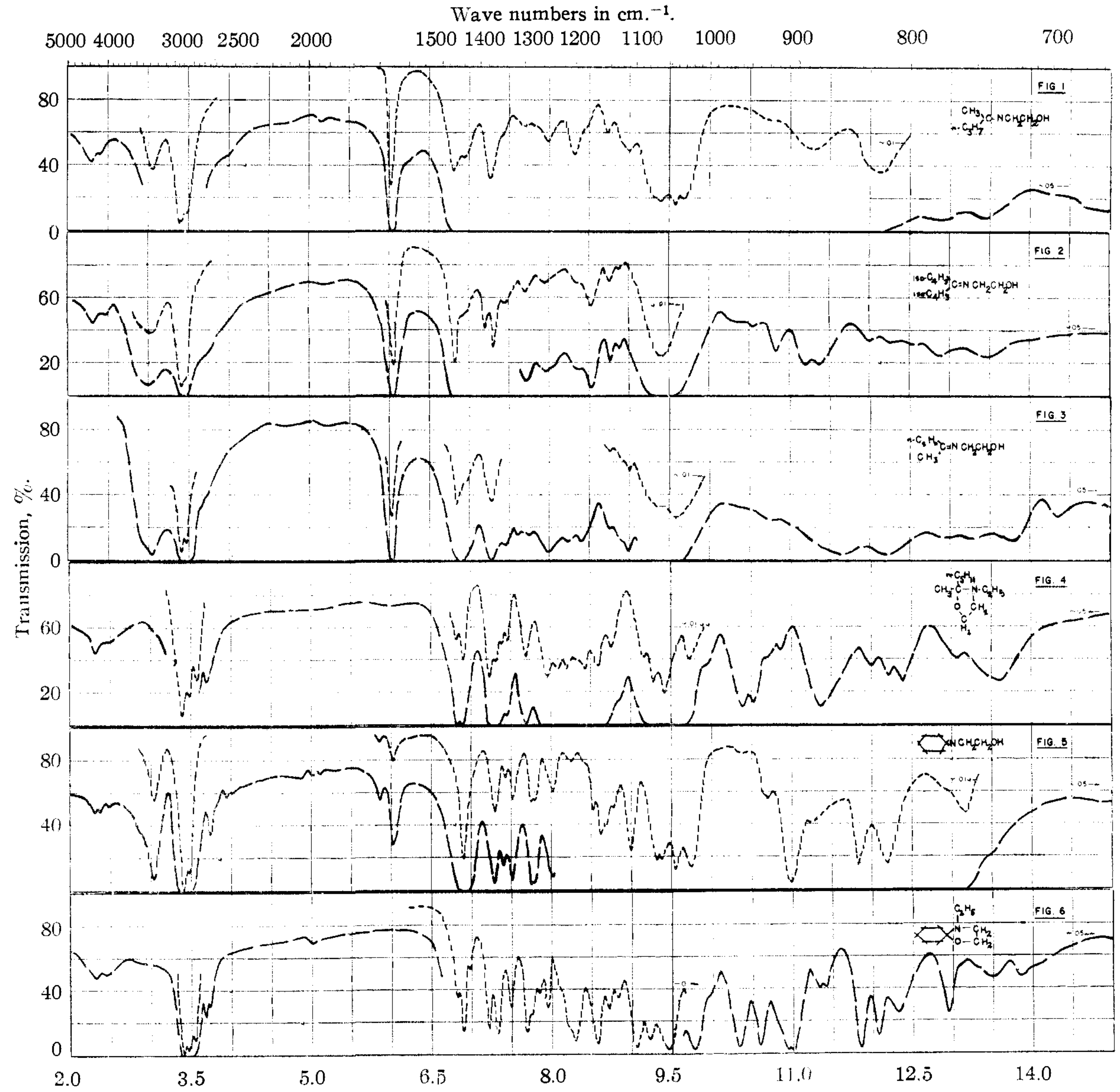
[1] The opinions contained herein are the author's and are not to be construed as official or reflecting the views of the Department of Navy. Article not copyrighted.

[2] L. W. Daasch and U. E. Hanninen, THIS JOURNAL, **72**, 3673 (1950).

[3] L. H. Goodson and H. Christopher, *ibid.*, **71**, 1117 (1949).

[4] A. C. Cope and E. M. Hancock, *ibid.*, **64**, 1503 (1942).

[5] (a) R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948); (b) H. W. Thompson, *J. Chem. Soc.*, 328 (1948).



Figs. 1–6.—Infrared spectra of some Schiff bases and oxazolidines: 1, N-1-methylbutylidenethanolamine; 2, N-1-isobutyl-3-methylbutylidenethanolamine; 3, N-1-methylhexylidenethanolamine; 4, 2-methyl-2-amyl-3-ethyloxazolidine; 5, N-cyclohexylidenethanolamine; 6, spirocyclohexane-1,2′-(3′-ethyl)-oxazolidine.

N-ethylethanolamine. The compounds obtained from the secondary amine probably have the oxazolidone structure[6]; at least the Schiff base structure is not possible. It is immediately obvious that the strong absorption around 1650 cm.$^{-1}$ in Figs. 1, 2, 3 and 5, which is absent in Figs. 4 and 6, is due to the C=N linkages in the Schiff base structures.[5]

Experimental

Technical grade starting materials were used without further purification. The compounds were all prepared by refluxing a solution of ketone, amine and benzene until the major part of the theoretical amount of water had been collected in an attached water trap. The product was separated from the reaction mixture by distillation and purified by several further distillations at reduced pressure. The physical constants of the materials obtained are given in Table I.

Simple distillations were not sufficient to separate the product in the reactions of cyclohexanone and methyl *n*-propyl ketone with N-ethylethanolamine. Purification by fractionation was successful only with the cyclohexanone reaction mixture. Diisobutyl ketone did not condense with N-ethylethanolamine, apparently due to the steric hindrance of the isobutyl groups to the formation of the oxazolidine ring.

Spectroscopic Equipment and Methods.—The spectra were obtained on a large prism spectrometer described in detail elsewhere.[7] Freshly distilled samples[8] were in stoppered absorption cells whose potassium bromide windows were separated by a spacer of appropriate thickness.

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(6) One might note the absence of absorption at 3300 cm.$^{-1}$ in Figs. 4 and 6 (no hydrogen bonded NH or OH groups) which may be interpreted as evidence that the compounds prepared from secondary amines *do* have the oxazolidine structure since any open chain compound such as RR′C(OCH$_2$CH$_2$NHC$_2$H$_5$)$_2$ would have this absorption band.

(7) J. Rud. Nielsen, F. W. Crawford and D. C. Smith, *J. Opt. Soc. Am.*, **37**, 296 (1947).

(8) The recording speed of the spectrograph was such that it required about four hours to obtain a complete spectrum.

TABLE I

MATERIALS AND PHYSICAL CONSTANTS

Reactants			B.p., °C.		
Ketone	Amine	Product	°C.	Mm.	$n^{25}D$
Methyl *n*-propyl	Ethanol-	N-1-Methylbutylidenethanolamine	91–95	60	1.4491
Diisobutyl	Ethanol-	N-1-Isobutyl-3-methylbutylidenethanolamine	153–155	80	1.4564
Methyl *n*-amyl	Ethanol-	N-1-Methylhexylidenethanolamine	88–89	6.5	1.4480
Methyl *n*-amyl	N-Ethylethanol-	2-Methyl-2-amyl-3-ethyloxazolidine	129–130	65	1.4420
Cyclohexanone	Ethanol-	N-Cyclohexylidenethanolamine	108–110	50	1.4819
Cyclohexanone	N-Ethylethanol-	Spirocyclohexane-1,2′-(3′-ethyl)-oxazolidine	107–109	80	1.4722

Acknowledgment.—The interest of Dr. D. C. Smith in this work and the preparation of N-1-methylhexylidenethanolamine by Mr. Urho E. Hanninen are greatly appreciated.

WASHINGTON, D. C.

RECEIVED MARCH 12, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

Spectrophotometric Study of Tetrabutylammonium Tribromide

BY ROBERT E. BUCKLES, ALEXANDER I. POPOV, WILLIAM F. ZELEZNY AND ROBERT J. SMITH

Crystalline tetrabutylammonium tribromide was prepared by two different methods. Its ultraviolet absorption spectrum was determined in ethylene chloride solutions. Such solutions were found to be relatively unstable because of the bromination of the solvent which was observed. The method of continuous variation and the slope-ratio method, applied to mixtures of the tetrabutylammonium bromide and bromine in various ratios of concentrations, both indicate that the tribromide was the only polyhalogen present in bromotrichloromethane solution. The equilibrium constant for the reaction: $(C_4H_9)_4NBr_3 \rightleftarrows (C_4H_9)_4NBr + Br_2$ at 25° in bromotrichloromethane was calculated to be 6.0×10^{-6}.

Polyhalides of organic molecules, especially those containing nitrogen, have been reported since the early days of organic chemistry. In many cases such compounds were prepared as solid derivatives of the parent compounds. Among the polyhalides which are often encountered are the quaternary ammonium polyhalides. Of these, the polyiodides and mixed polyhalides containing iodine are the most common. Less well known are the quaternary ammonium polybromides. Phenyltrimethylammonium tribromide[1] and pentabromide,[2] *p*-tolyltrimethylammonium tribromide[2] and pentabromide,[2] a number of other substituted phenyltrimethylammonium tribromides,[3] and tetramethylammonium tribromide[4] have been isolated as pure solids. Solid higher polybromides which exhibited fairly high bromine pressures have also been reported, but the compositions were variable. Solids whose analyses corresponded to the formulas: $(C_2H_5)_4NBr_9$,[5] $(CH_3)_4NBr_9$,[4b] $(CH_3)_4NBr_{11}$[5] and $(CH_3)_4NBr_{13}$,[4a] have been obtained. In the latter case the solid was reported to lose bromine easily on standing to yield the crystalline tribromide.

Although the stability of these solids has been observed no study of the stability of the polybromides in solution has been made. The ultraviolet absorption spectra of cesium tribromide and of *p*-bromophenyltrimethylammonium tribromide have been measured in water and in alcohol.[6] Although the spectra obtained were characteristic of species other than just the monobromides and bromine originally present, the actual compositions of the absorbing species in solution were not determined. In the present work a spectrophotometric study of the nature of the absorbing species has been made on the tetra-*n*-butylammonium bromide–bromine system in solution.

Experimental

Tetra-*n*-butylammonium Bromide.—This material was kindly supplied by Dr. Mervin Runner of this Laboratory. The solid had been recrystallized from anhydrous ethyl acetate and from benzene to give a product of m.p. 116–116.5°.[7] The m.p. reported is 103.1–103.3°.[8]

Preparation of Tetra-*n*-butylammonium Tribromide.—A solution of 0.40 g. (0.0012 mole) of tetrabutylammonium bromide in 25 ml. of carbon tetrachloride was mixed with 25 ml. of 0.05 *M* bromine in carbon tetrachloride. The immediate light orange precipitate was filtered to yield 0.54 g. (91%) of the tribromide, m.p. 70–72°.

An alternate method of synthesis involved allowing an excess of bromine vapor to come in contact with 0.50 g. (0.0016 mole) of solid tetrabutylammonium bromide for three hours. The excess bromine adsorbed was allowed to evaporate. The orange solid was washed repeatedly with carbon tetrachloride. A yield of 0.63 g. (84%) of the tribromide, m.p. 70–72°, was obtained. A mixture of the two preparations had the same m.p.

It was possible to crystallize the products of these preparations from glacial acetic acid–carbon tetrachloride. The m.p. of the resultant orange needles was 72.5–74.0°. Attempts to crystallize the product from aqueous alcohol were unsuccessful because the tribromide was reduced by the alcohol. The characteristic orange color of the solution gradually disappeared even in the cold.

Methods of Analysis of Tetrabutylammonium Tribromide.—Total bromine was determined gravimetrically after being converted to bromide ion. A weighed sample of the tribromide was dissolved in 85–90% ethanol saturated with sulfur dioxide. The solution was warmed on the steam-bath for several minutes, and then two or three drops of 6 *N* nitric acid was added. The gravimetric determina-

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(1) J. Tafel, *Ber.*, **31**, 1349 (1898).

(2) K. Fries, *Ann.*, **346**, 217 (1906).

(3) D. Vorlander and E. Siebert, *Ber.*, **52**, 283 (1919); H. McCombie and T. H. Reade, *J. Chem. Soc.*, **123**, 141 (1923).

(4) (a) F. D. Chattaway and G. Hoyle, *ibid.*, **123**, 654 (1923); (b) L. Farkas and O. Schächter, THIS JOURNAL, **71**, 2252 (1949).

(5) E. J. Bowen and A. W. Barnes, *Chemistry and Industry*, 254 (1945).

(6) F. L. Gilbert, R. R. Goldstein and T. M. Lowry, *J. Chem. Soc.*, 1092 (1931).

(7) All m.p.'s corrected.

(8) R. L. McIntosh, D. J. Mead and R. M. Fuoss, THIS JOURNAL, **62**, 506 (1940).