

Studies in the Stereochemistry of Quinquevalent Nitrogen. IV.

By

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I.

The Absorption Spectra of Quaternary Ammonium Compounds.

In an organic compound, isomers, caused by a difference of the configuration of atoms or atomic groups in the molecule, give similar ultra-violet absorption spectra; while those caused by a difference in the structure in the molecules, such as keto and enol forms, give dissimilar spectra.¹

The author, in his II. article,² has shown that in the optically active methyl allyl phenyl benzyl ammonium compounds there exist optical isomers in α and γ forms which were assumed to be stereoisomers arising from the different configurations of the atomic groups in their molecules. This hypothesis was partly supported by the experiments³ of autoracemisation conducted on these two isomers; but further confirmation was wanted.

¹ B. Hartley, J. Chem. Soc., **47**, 685 (1885); **77**, 840 (1900); Baly and Desch, *Ibid.*, **85**, 1029 (1904); Baly and Collie, *Ibid.*, **87**, 1343 (1905); Baly and Ewbank, *Ibid.*, **87**, 1355 (1905); Baly, Tuck and Marsden, *Ibid.*, **97**, 571 (1910); Purvis, *Ibid.*, **97**, 1553 (1910); Stewart, *Ibid.*, **91**, 1537 (1907); Hantzsch, Ber. D. Chem. Ges., **43**, 1651 (1910); Ley and Ulrich, *Ibid.*, **42**, 3441 (1909).

² Mem. Coll. Sci., Kyoto, **1**, 123 (1915).

³ *Ibid.*, **1**, 231 (1915).

Recently interesting observations with regard to the nature of the valency of cobalt atom were made by Rutter and Nikolopoulos¹ and also by Dr. Shibata² from a study of the absorption spectra of a cobalt complex.

Then, it was thought that a study of the ultra-violet absorption spectra of a quaternary ammonium compound might throw some light upon the combining way of atomic groups of pentavalent nitrogen atom and also upon the nature of the five valencies; and the present investigation was undertaken.

In the experiments, the absorption spectra of the compound were photographed with a quartz spectrograph from Adam Hilger, of N/100 and N/1000 solutions, changing the thicknesses of each solution from 100 to 1 mm. The source of the ultra-violet rays was obtained with an arc from iron electrodes.

The absorption curve was plotted from the photograph as usual, according to Hartley-Baly's method.³

EXPERIMENTAL PART.

1. *Hydrochlorides of ψ Cumidine and Benzyl Amine.*

According to Hartley⁴ and Baly,⁵ the author studied the ultra-violet absorption spectra of hydrochlorides of ψ cumidine and benzyl amine from Kahlbaum in the presence of hydrochloric acid to prevent the hydrolysis of the salts in their dilute aqueous solutions.

Under this condition, N/100 and N/1000 solutions of the salts gave the continuous absorption curves, as seen in Fig. I.

The salts persist in two absorption bands; and the heads of the bands were in ψ cumidine at about $1/\lambda$ 3500 and $1/\lambda$ 3700 and in benzyl amine $1/\lambda$ 3500 and $1/\lambda$ 4000 respectively.

¹ Z. Phys. Chem., **82**, 361 (1913).

² J. Coll. Sci., Tokyo. **37**, 1 (1915); G. Urbain and Y. Shibata, Compt. rend., **157**, 593 (1913).

³ J. Chem. Soc., **85**, 1029 (1904).

⁴ *Loc. cit.*

⁵ *Loc. cit.*

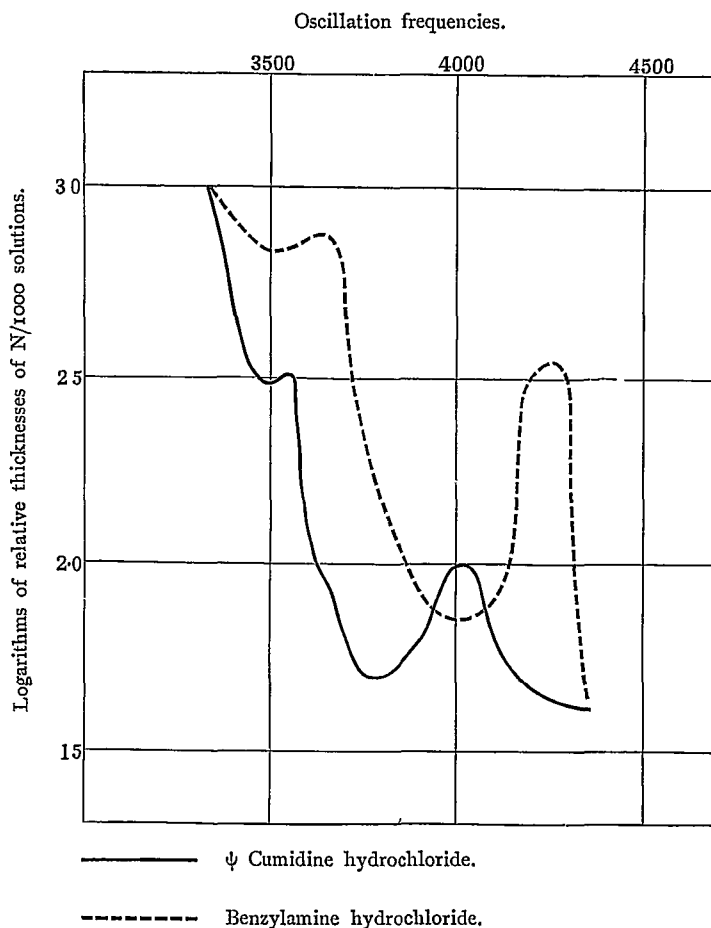
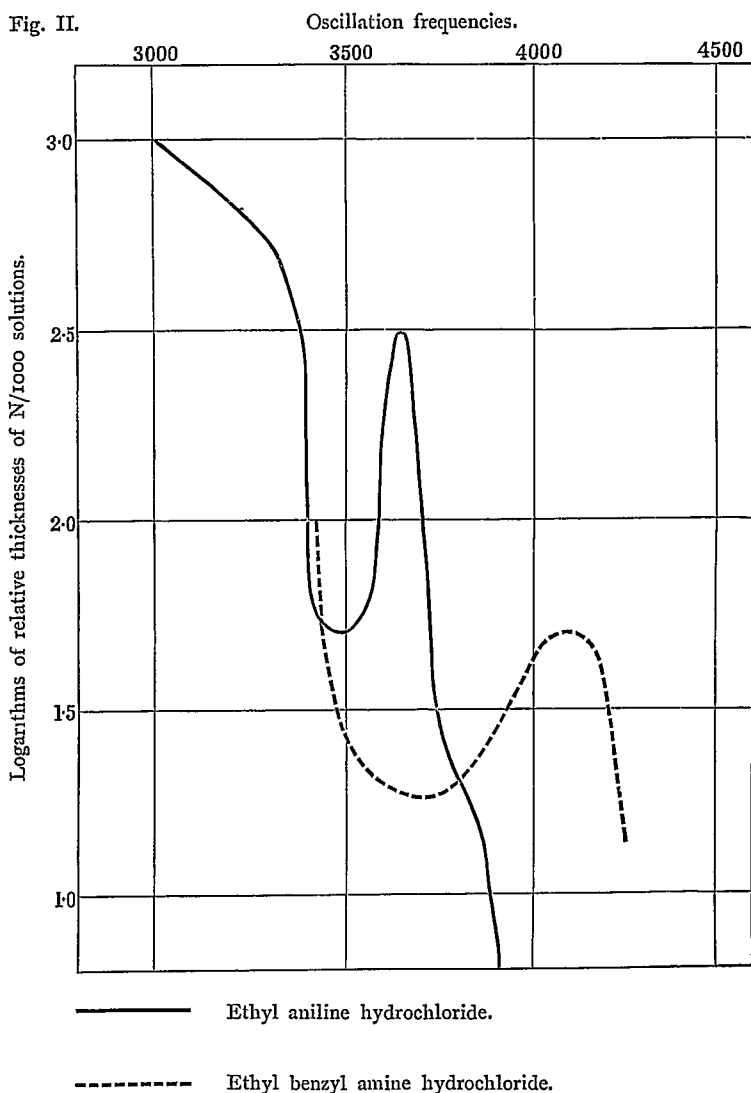


Fig. I.

2. *Hydrochlorides of Ethyl Benzyl Amine and Ethyl Aniline.*

The absorption spectra of the ultra-violet regions of N/100 and N/1000 solutions of these salts in the presence of an excess of hydrochloric acid have been studied, and the results are shown in Fig. II.

It will be noticed that there is only one absorption band in these secondary amine hydrochlorides and also that its position is more towards the red end of the spectrum than is that of the primary amine salt, the head of the band being about $1/\lambda$ 3500— $1/\lambda$ 3600.



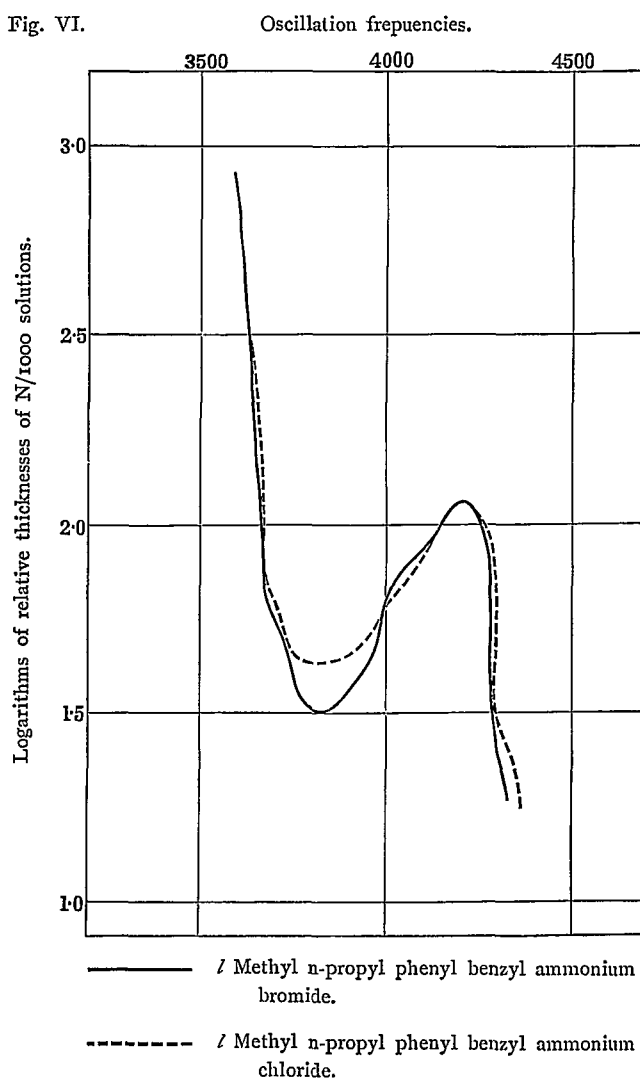
3. *α* Dextro Methyl Allyl Phenyl Benzyl Ammonium Dextro Camphorsulphonate, *α* Dextro Methyl Allyl Phenyl Benzyl Ammonium Bromide and *γ* Dextro Methyl Allyl Phenyl Benzyl Ammonium Dextro Camphorsulphonate.

N/100 and N/1000 aqueous solutions of these substances, prepared by the author, were studied and the photographs are shown in Plates I, II & III; from which their absorption curves have been drawn as shown in Fig. III.

4. *Laevo Methyl n-Propyl Phenyl Benzyl Ammonium Bromide and Laevo Methyl n-Propyl Phenyl Benzyl Ammonium Chloride.*

The absorption spectra of these substances, prepared by the author, were studied N/100 and N/1000 aqueous solutions gave a continuous absorption curve of similar form as seen in Fig. IV.

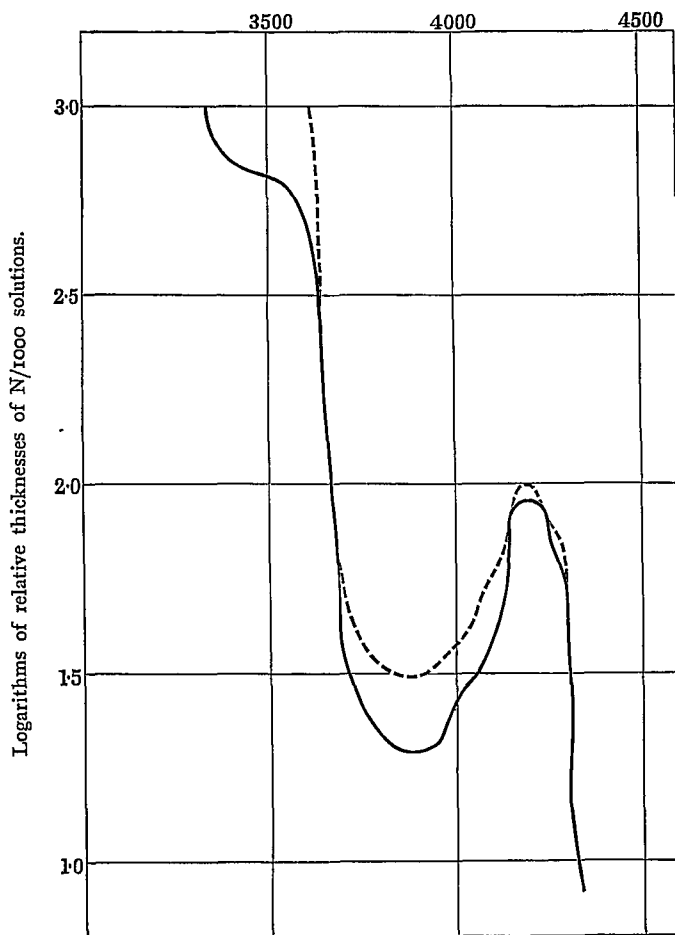
The band was as strongly persistent as that of the other quaternary ammonium salts, the head being about $1/\lambda$ 3800.



5. *Methyl Phenyl Benzyl Ethyl Acetate Ammonium Bromide*
and Methyl Phenyl Benzyl Ethyl Acetate Ammonium
Dextro Camphorsulphonate.

To see what change might take place in the absorption spectra by the substitution of the $\text{CH}_2\text{COOC}_2\text{H}_5$ group for the allyl group in the

Fig. V. Oscillation frequencies.



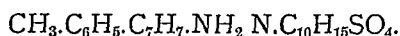
———— Methyl phenyl benzyl ethyl acetate ammonium
d camphorsulphonate.
 - - - - - Methyl phenyl benzyl ethyl acetate ammonium
 bromide.

quaternary ammonium compound above mentioned, the author prepared these substances and studied their absorption spectra in N/100 and N/1000 aqueous solutions.

The photograph of the absorption spectra of the camphorsulphonate is shown in plate IV.; and then plotted curve in Fig. V.

The absorption spectra of the ultra-violet rays as seen in Fig. V and plate IV, exhibit a characteristic band for the quaternary ammonium compound and by the substitution of the atomic group suffer no change. The absorption band is strongly persistent, and its head about $1/\lambda$ 3900.

6. *Methyl Phenyl Benzyl Hydrazonium Dextro Camphorsulphonate,*



Nitroso methyl aniline, prepared according to Hepp¹ and Fischer² from methyl aniline from Kahlbaum and nitrous acid, was reduced to methyl phenyl hydrazine.³

Methyl phenyl hydrazine was purified by transforming it to its sulphate. The sulphate was analysed with the following result:

0.3335 grm. sulphate gave 0.2092 grm. BaSO₄.

	Calc. for C ₁₇ H ₁₀ N ₂ .H ₂ SO ₄ .	Found.
Sulphur	9.19	8.53

Methyl phenyl benzyl hydrazonium iodide was obtained, by the method suggested B. K. Singh⁴ from methyl phenyl hydrazine and benzyl iodide, and was purified by recrystallization from its aqueous solution. The iodide was found to melt at 122–123°. The analysis of the substance was as follows:

0.2504 grm. substance give 0.1740 grm. AgI.

	Calc. for C ₁₄ H ₁₇ N ₂ I.	Found.
Iodine	37.35	37.56

To an ethyl acetate solution of methyl phenyl benzyl hydrazonium iodide was added one molecular proportion of dry dextro silver camphorsulphonate; and the methyl phenyl benzyl hydragonium dextro camphor-

¹ Ber. D. Chem. Ges., 10, 329 (1877).

² Lieb. Ann., 190, 151 (1878).

³ Fischer, *Ibid.*, 190, 152 (1878).

⁴ J. Chem. Soc., 105, 1972 (1914).

sulphonate thus formed was purified by recrystallization from ethyl acetate solution. The camphorsulphonate crystallizes in white needles from ethyl acetate solution, and melts at 168–169°.

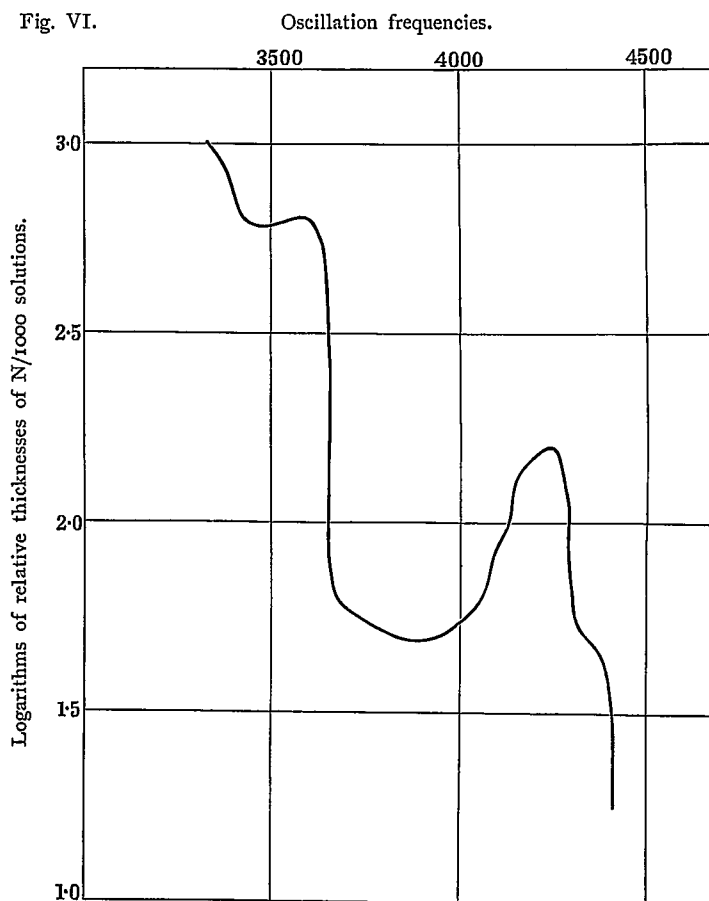
0.2165 grm. substance give 0.1095 grm. BaSO₄.

	Calc. for C ₂₁ H ₃₂ O ₄ N ₂ S.	Found.
Sulphur	7.21	6.95

The salt as seen from its properties and analysis, is identical with that obtained by Singh.¹

On N/100 and N/1000 aqueous solutions of the salt the absorption spectra were studied and the result is shown in Fig. VI and Plate V.

Fig. VI.



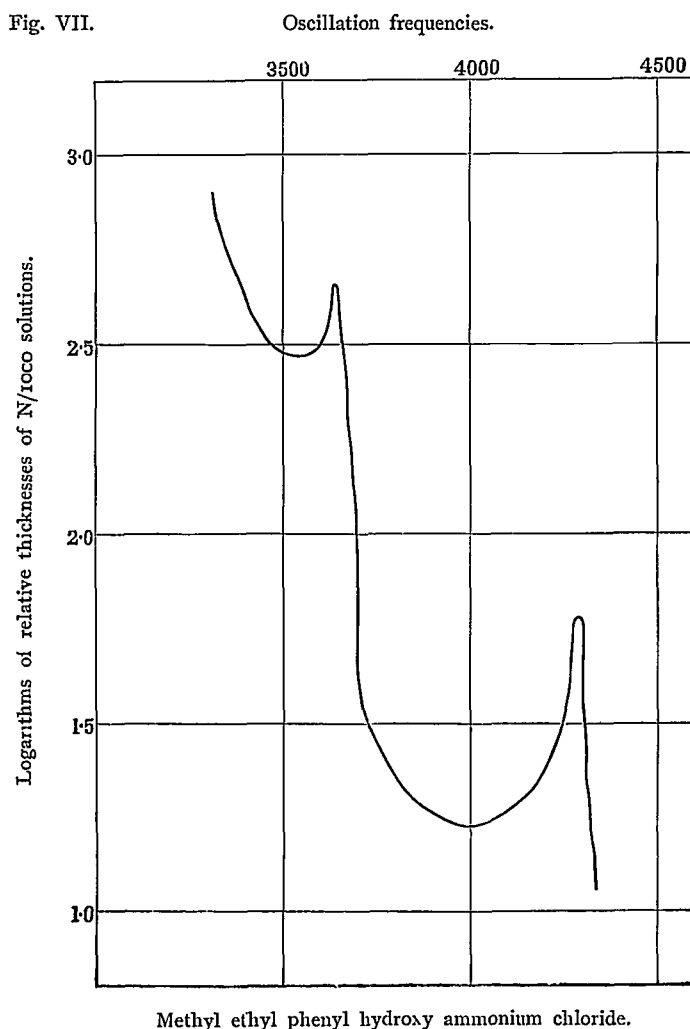
Methyl phenyl benzyl hydrazonium *d* camphorsulphonate.

¹ *Loc. cit.*

The general form of the absorption curve is like that of the other quaternary ammonium salts, but the substitution of the NH_2 group for the alkyl group caused a little shift of the absorption band towards the violet end of the spectrum.

7. *Methyl Ethyl Phenyl Hydroxy Ammonium Chloride.*

N/100 and N/1000 aqueous solutions of the substance, prepared by the author (see experimental part of section II.), exhibit two ab-



sorption bands as seen in Fig. VII. and Plate VI. The heads of the bands are about $1/\lambda$ 3500 and $1/\lambda$ 4000. The alteration in the position of the bands and in the form of the curve must be due chiefly to the substitution of OH group for an alkyl group in the ammonium compound.

SUMMARY.

1. The absorption spectra of the ultra-violet rays of the quaternary ammonium compounds derived from aniline are independent of the atom or atomic group (with exception of iodine) combined with negative valency to the nitrogen atom.

2. The substitution of an alkyl group such as ethyl, propyl, allyl or benzyl or of $\text{CH}_2\text{COOC}_2\text{H}_5$ group for one of the methyl groups in trimethyl phenyl ammonium compounds, causes no apparent change in the absorption curve; while the introduction of an hydrogen atom, OH group or NH_2 group causes an alteration in its form and position.

3. The absorption spectra of ammonium compounds depend upon the nature of the atomic group combined with positive valency to the nitrogen.

4. In a quinquevalent nitrogen atom four "negative" valencies have a nature different from that of the fifth valency by which a negative atom or atomic group is combined to the nitrogen.

5. The isomers in methyl allyl phenyl benzyl ammonium compound should be stereoisomers but not structure isomers.

II.

Non-equivalence of the Five Valencies of Pentvalent Nitrogen.

In the previous section the author proved that the fifth "positive" valency of the nitrogen atom is different from the four "negative" valencies in a study of the absorption spectra of the ammonium compound.

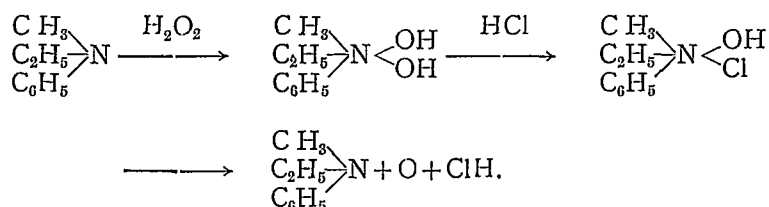
In order to get further confirmation of this conclusion from chemical reactions, the following experiments were carried out.

Some years ago Meisenheimer¹ prepared pairs of isomerides of the types $(\text{CH}_3)_3\text{N} \begin{smallmatrix} \text{OR} \\ \text{OH} \end{smallmatrix}$ and $(\text{CH}_3)_3\text{N} \begin{smallmatrix} \text{OH} \\ \text{OR} \end{smallmatrix}$ from trimethyl amine oxide, and

¹ Ber. D. Chem. Ges, 33, 1617 (1900).

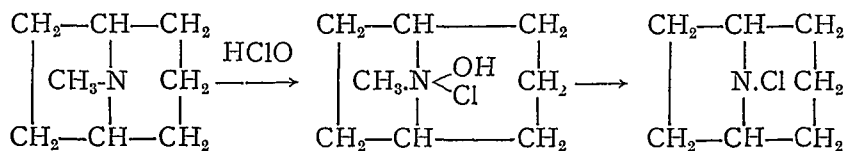
from a study of the decomposition products of these compounds presented important evidence upon the subject.

The author prepared methyl ethyl phenyl amine oxide according to Meisenheimer¹ from methyl ethyl aniline and hydrogen peroxide, and converted into methyl ethyl phenyl hydroxy ammonium chloride. The latter substance was subjected to distillation and was found to decompose into methyl ethyl aniline and hydrogen chloride. The mechanism of the reactions was assumed to be :



Furthermore, by the action of hypochlorous acid on methyl ethyl aniline, the author obtained a secondary amine as one of the reaction products, which assumed to be ethyl trichloro aniline.²

Willstätter and Iglauer³ have shown that chloronortropidine was formed on adding tropidine to an aqueous solution of hypochlorous acid, and the following words are found in their article „Die Einwirkung der unterchlorige Säure haben wir zu untersuchen begonnen bei tertiären, aliphatischen Basen, bei cyclischen Basen (N-Methylpiperidin, Tropan, Tropidin) und bei aromatischen Aminen ; das Dimethyl anilin liefert ein stechend riechendes, unbeständiges Oel, wahrscheinlich Methylphenylchlorostickstoff, welcher sich rasch durch Wanderung der Halogens in den Kern umwandelt,.....“.



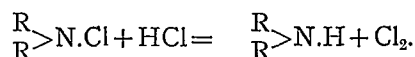
Breg⁴ had already noticed that dialkyl chloroimide yields dialkyl amine upon the passing of dry hydrochloric acid upon its solution.

¹ Ber. D. Chem. Ges., 41, 3966 (1908).

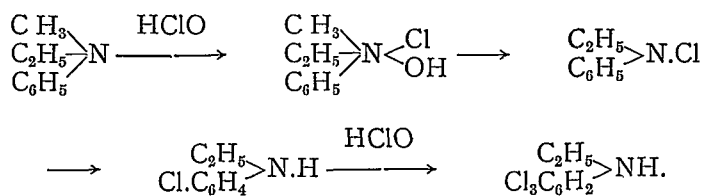
² Chem. Zentralbl., 78, I, 682 (1907).

³ Ber. D. Chem. Ges., 33, 1638 (1900).

⁴ A. ch., [7] 3289 (1894).



Infering from these facts, the author is led to believe that, in the present case methyl ethyl phenyl chloro ammonium hydroxide, a stereoisomer of methyl ethyl phenyl hydroxy ammonium chloride is first formed, which yields ethyl phenyl chloroamine with the elimination of methyl alcohol. The amine transformed by the rearrangement of chlorine atom from nitrogen to a carbon atom of benzene nuclear into ethyl chloroaniline, finally reacting with an excess of hypochlorous acid, yields ethyl trichloroaniline; thus the course of the reactions should be represented by the following scheme :



EXPERIMENTAL PART.

1. *Decomposition of Methyl Ethyl Phenyl Hydroxy Ammonium Chloride.*

Methyl ethyl phenyl amine oxide, prepared by the oxidation of methyl ethyl aniline from Kahlbaum with 3% hydrogen peroxide, was purified by transforming into its picrate. The picrate was found to melt at 143–144°, though Meisenheimer gave 147–148° for its melting point. The result of the analysis was as follows :

0.1276 gm. picrate gave 0.2228 gm. CO₂ and 0.0577 gm. H₂O.

	Calc. for C ₁₅ H ₁₆ O ₃ N ₄ .	Found.
Carbon	47.37	47.62
Hydrogen	4.21	5.01

The picrate treated with conc. hydrochloric acid and pure methyl ethyl phenyl hydroxy ammonium chloride was obtained by crystallization from a chloroform-benzene solution.

The substance was analysed, and its chlorine content was determined.

¹ *Loc. cit.*

0.138 gm. substance gave 0.1066 gm. AgCl.

	Calc. for $C_9H_{14}ONCl$.	Found.
Chlorine	18.94	19.12

When an aqueous solution of methyl ethyl phenyl hydroxy ammonium chloride was subjected to distillation, methyl ethyl aniline was obtained, as ascertained by analysis, and the melting point determination of the picrate.

0.1268 gm. amine picrate gave 0.2273 gm. CO_2 and 0.0604 gm. H_2O .

	Calc. for $C_{15}H_{15}O_7N_4$.	Found.
Carbon	49.59	49.12
Hydrogen	4.13	5.29

The same amine was also obtained by the decomposition of methyl ethyl phenyl amine oxide.

2. Ethyl Trichloroaniline, $C_2H_5Cl_3C_6H_2NH$.

To an aqueous solution of methyl ethyl aniline hydrochloride an excess of hypochlorous acid, prepared by the method of Erlenmyer and Lipp,¹ was added with constant stirring. When the reaction was ended, the oily product, deposited on the bottom of the vessel, was separated from the mother liquor by decantation. The substance was treated with caustic soda and water successively and extracted with ether. The ethereal solution, dried with anhydrous sodium sulphate, was distilled to remove the solvent; and the residue was subjected to fractional distillation in vacuum. The fraction which boils between $127-130^\circ$ at 15 mm is an yellow oil with an unpleasant odour.

I. 0.2482 gm. substance gave 0.4 gm. CO_2 and 0.1091 gm. H_2O .

II. 0.2026 gm. substance gave 0.3201 gm. CO_2 and 0.0811 gm. H_2O .

III. 0.3389 gm. substance gave 0.5842 gm. AgCl.

	Calc. for $C_8H_8NCl_3$.	Found.		
		I	II	III
Carbon	42.76	43.95	43.09	—
Hydrogen	3.56	4.88	4.14	—
Chlorine	47.44	—	—	42.67

¹ Leib. Ann., 219, 185 (1883).

The substance, which is neither primary amine nor tertiary amine, yields a platinum double salt which melts at 180–181°.

The analytical result of the platinum double salt was as follows:
0.1013 grm. platinum double salt gave 0.0239 grm. Pt on ignition.

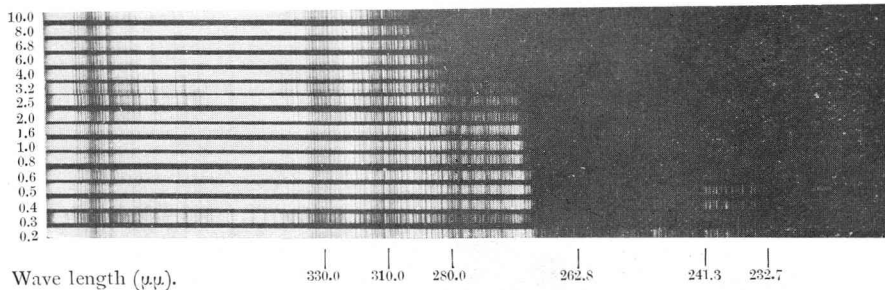
	Calc. for $C_{16}H_{18}N_2Cl_{12}Pt$.	Found.
Platinum	22.70	23.57

In conclusion, the author wishes to express his thanks to Asst.-Prof. Yuji Shibata, of Tokyo Imperial University, for his kind help in preparing the absorption spectra in this work.

Pt. I.

Thickness
(cm.)

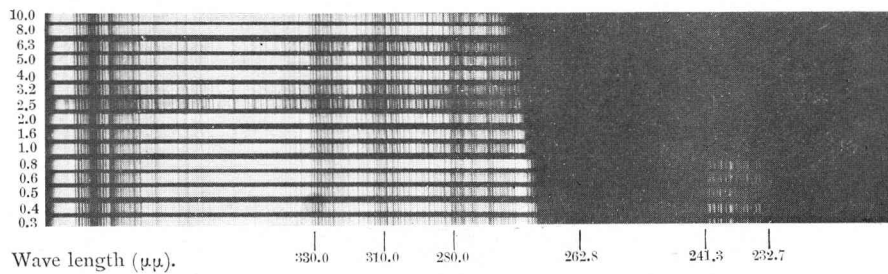
α d Methyl allyl phenyl benzyl amm. d camphorsulphonate, $\frac{1}{100}$ N.



Pt. II.

Thickness
(cm.)

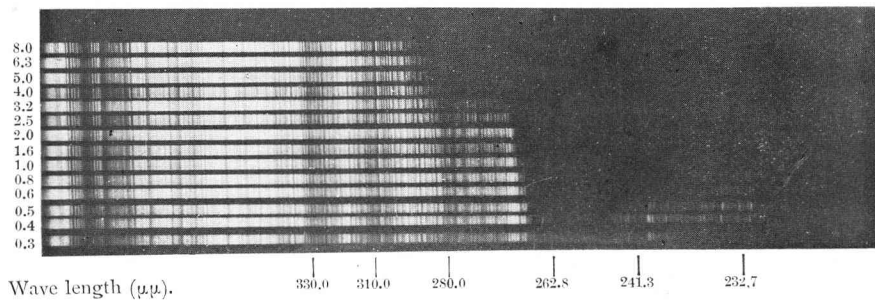
α d Methyl allyl phenyl benzyl amm. bromide, $\frac{1}{100}$ N.



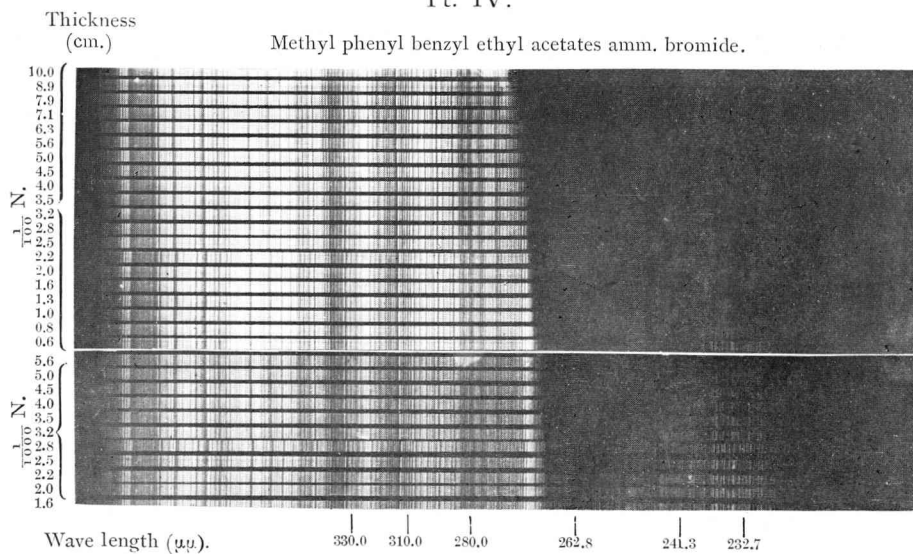
Pt. III.

Thickness
(cm.)

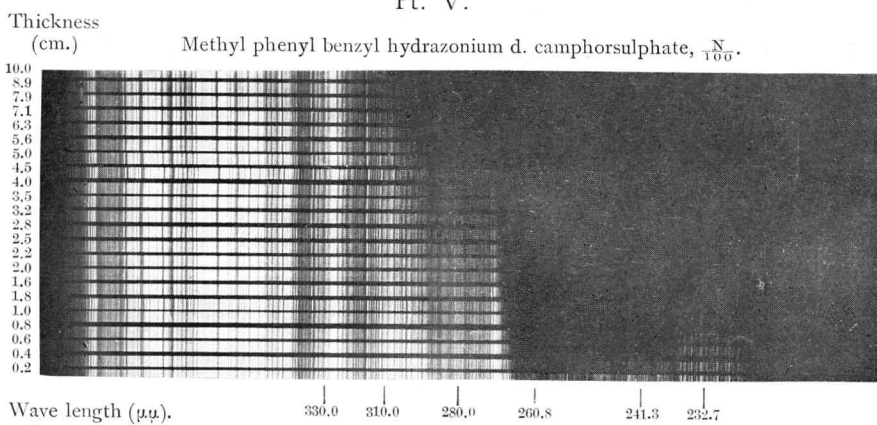
γ d Methyl allyl phenyl benzyl amm. d camphorsulphonate, $\frac{N}{100}$



Pt. IV.



Pt. V.



Pt. VI.

