

# Studies in the Stereochemistry of Quinquevalent Nitrogen. III.

Autoracemisation of Optically Active Ammonium Compounds.

By

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Autoracemisation of optically active ammonium compounds was first observed by Pope and Harvey<sup>1</sup> with dextro methyl allyl phenyl benzyl ammonium iodide in its chloroform solution, and since then the study of its cause and mechanism has been attempted by many investigators, but the problem has not been solved yet.

It has been known that racemisation of ammonium compounds occurs almost always in the solvents of a small dielectric constant<sup>2</sup> such as chloroform, bromoform, carbon bisulphide and benzene, which stand in a close connection with the chemical nature of the atoms or atomic groups linked to the nitrogen atom<sup>3</sup>, and again that the velocity of reaction is facilitated by the influence of light and heat.<sup>4</sup>

The different hypothesis put forward by the different investigators, for the explanation of the mechanism of autoracemisation will be stated below :

## 1. *Permutation Theory.*

H. Goldschmidt<sup>5</sup> is of an opinion that the racemisation of ammonium compounds may be caused by the permutation of the positions of atomic groups linked to the nitrogen within the molecule, as in the case of tautomeric change, and has proposed a following theoretical

<sup>1</sup> J. Chem. Soc., **91**, 828 (1901).

<sup>2</sup> Jones: *Ibid.*, **87**, 135 (1905); **89**, 281 (1906); Wedekind: Ber. D. Chem. Ges., **38**, 343, 3933 (1905); **39**, 478 (1906); Z. Electrochem., **12**, 331 (1906); Halban: Ber. D. Chem. Ges., **41**, 2417 (1908).

<sup>3</sup> Jones: J. Chem. Soc., **89**, 281 (1906); Wedekind and Paschke: Ber. D. Chem. Ges., **44**, 1406 (1911).

<sup>4</sup> Pope: J. Chem. Soc., **75**, 1127 (1899); **79**, 828 (1901); Jones: *Ibid.*, **87**, 135 (1905); **89**, 281 (1906); Wedekind: Z. Phys. Chem., **45**, 242 (1903); Wedekind and Paschke: Ber. D. Chem. Ges., **41**, 1029 (1908); Halban: *Loc. cit.*

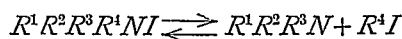
<sup>5</sup> Z. Electrochem., **12**, 416, 516 (1906); Le Bell: Compt. rend., **130**, 1552 (1900).

expression based upon a thermodynamical principle, explaining the mechanism of reaction :

$$A = 2RT \ln 2.$$

### 2. *Dissociation Theory.*

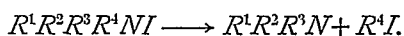
Pope<sup>1</sup>, drawing a conclusion from his experimental results, has attributed the phenomena of racemisation to the dissociation of ammonium compounds into alkyl haloid and tertiary amine and to their subsequent recombination, resulting eventually in equilibrium with the formation of equal quantities of the dextro and lævo isomerides, as will be shown in the following scheme :



and he also declares that heat and light, and a basic radical attached to nitrogen atom such as an allyl or benzyl group have to promote the tendency of dissociation.

### 3. *Decomposition Theory.*

In the molecular weight determination of methyl allyl phenyl benzyl ammonium iodide in chloroform solution by the microscopic method, carried out by Barger,<sup>2</sup> Halban<sup>3</sup> has been induced to the notion that optically active ammonium compounds, decompose in their racemisation into tertiary amines and alkyl haloides as will be shown in the following scheme :



Such hypothesis has been confirmed by determining the amounts of ammonium salts remained without decomposition, in the chloroform solutions which decrease in proportion to the duration of time, by titration with the standard silver nitrate solution.

Wedekind,<sup>4</sup> also denies the dissociation and permutation theories and supports Halban's explanation inferring from the molecular weight determination by the cryoscopic method in a benzene solution, the conductivity measurement of the ammonium salt solutions and the comparative determination of their optical rotations.

Now, allowing a chloroform solution of methyl allyl phenyl ben-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> J. Chem. Soc., 85, 315 (1904).

<sup>3</sup> Z. Eleck. Chem., 13, 57 (1907); Ber. D. Chem. Ges., 41, 2417 (1908).

<sup>4</sup> Ber. D. Chem., Ges., 41, 2689 (1908); 44, 1406, 3078 (1911).

zyl ammonium iodide, as observed by Wedekind and Paschke<sup>1</sup> to stand, it changed gradually yellow emitting the characteristic odour of benzyl iodide, and these facts seem to give a support to the decomposition theory by Halban. In order to determine the true nature of autoracemisation of optically active ammonium compounds, and if possible, to decide the cause of such a phenomenon the author has undertaken the present investigation.

### *I. Mechanism of the Autoracemisation.*

For studying the nature of the reaction, the author has examined the velocity of the racemisation of the ammonium iodides in chloroform solutions at 25° with polarimeter, and calculated the velocity-constants as the monomolecular reaction by the following formula :

$$k = \frac{1}{t} \log \frac{a_0}{a} = \frac{1}{t} \log \frac{1}{1-x}$$

where  $a_0$  denotes the initial rotatory power,  $a$  one at any time  $t$  and  $x = \frac{a_0 - a}{a_0}$ .

As seen in the experimental results shown in the tables I, II, IV and V, the velocity constants of  $\alpha$  and  $\gamma$  dextro methyl allyl phenyl benzyl ammonium iodides are same, and also coincide with those observed by Wedekind<sup>2</sup> by the same method, but not with Halban's observation.<sup>3</sup> Further, the constant of dextro methyl *n*-propyl phenyl benzyl ammonium iodide was found to be same with that of Wedekind.<sup>4</sup>

Infering the nature of racemisation from the reaction velocity it may belong to an intramolecular reaction<sup>5</sup> which is considered as a self-decomposition or dissociation of molecule. The fact that the racemisation constants of  $\alpha$  and  $\gamma$  dextro methyl allyl phenyl benzyl ammonium iodides in chloroform solution are identical, while their specific rotations are different, would furnish a support to the decomposition theory.

For the confirmation of such a view, the author has examined the absorption spectra, in the ultraviolet rays, of a chloroform solution

<sup>1</sup> Ber. D. Chem. Ges 43, 1303 (1910).

<sup>2</sup> Z. Elect. Chem., 12, 332 (1906); Ber. D. Chem. Ges., 41, 1029 (1908).

<sup>3</sup> Z. Elect. Chem., 13, 57 (1907).

<sup>4</sup> Ber. D. Chem. Ges., 41, 2659 (1908).

<sup>5</sup> E. Wedekind: Die Entwicklung der Stereochemie des funtwertigen Stickstoffs in letzten Jahrzehnt, 1909. s 33.

of freshly prepared dextro methyl allyl phenyl benzyl ammonium iodide, the same solution which has been allowed to stand for a day and a solution of methyl allyl aniline which is supposed as one of the decomposition products of the above iodide, all under the same condition, and actually the results of experiment, as shown in Fig. 1, seem to realise our view.

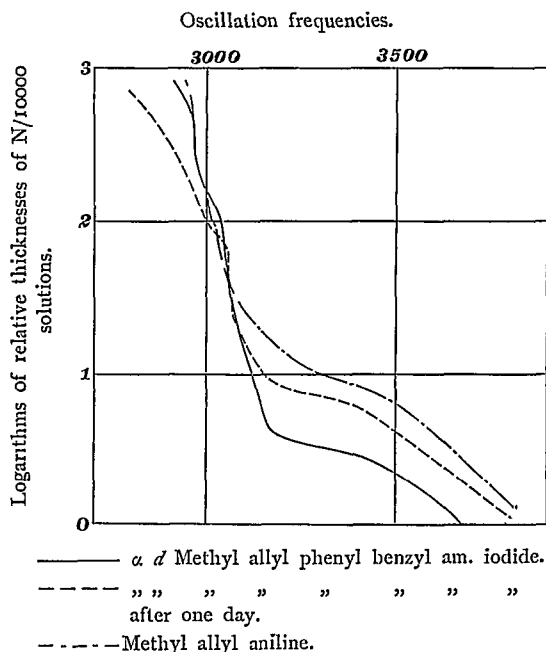
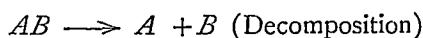
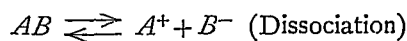


Fig. 1.

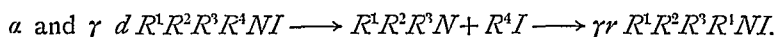
Theoretically it may be assured that when substance  $AB$  dissociates into  $A$  and  $B$  there may still exist a kind of chemical affinity between them on account of their reversibility, being different from decomposition :



Now extending the above view for the racemisation of ammonium compounds and taking an account the decomposition phenomena of the ammonium bases by heat<sup>1</sup> for the consideration, it is highly

<sup>1</sup> Mem. Coll. Sci. Engin., Kyoto. 3, 371 (1912).

probable that when  $\alpha$  and  $\gamma$  dextro methyl allyl phenyl benzyl ammonium iodides are dissolved in chloroform, each gradually decomposes into methyl allyl aniline and benzyl iodide, and the decomposition products, in a greater part, recombine to the same ammonium iodide, that is,  $\gamma$  methyl allyl phenyl benzyl ammonium iodide, respectively.



When a chloroform solution of  $\alpha$  methyl allyl phenyl benzyl ammonium iodide was set aside for 3 days in a laboratory, it changed orange yellow in colour, and after distilling off the solvent there was found to remain a brownish orange viscous residue which on standing for a few days produced a crystalline mass consisting of methyl allyl phenyl benzyl ammonium iodide. The substance thus formed was made to crystallize from alcohol and subjected to resolution with anhydrous silver camphorsulphonate as usual. The reaction product recrystallized from acetone was observed to show  $[\alpha]_D^{25} = +51.0^\circ$  for its specific rotatory power in an aqueous solution.

In the second experiment,  $\alpha$  methyl allyl phenyl benzyl ammonium iodide was heated to boil in chloroform solution at  $62^\circ$  for 2 days, and a dark brown syrupy substance obtained from the solution was confirmed to consist of methyl allyl aniline and benzyl iodide.

Pure methyl allyl phenyl benzyl ammonium iodide isolated from the above dark brown syrupy substance was mesotomized with silver dextro-camphorsulphonate into two optical antipodes, and the purified dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate melting at  $162-163^\circ$ , gave the same specific rotatory power  $[\alpha]_D^{25} = +56.48^\circ$  as that of  $\gamma$  isomeride.

In the third experiment, the raw dextro methyl allyl phenyl benzyl ammonium iodide heated to boil in its chloroform solution at  $62^\circ$  for 3 days, was converted into racemic ammonium iodide which was identified after resolution, by its rotatory power of camphorsulphonate.

On the other hand the author has treated the  $\gamma$  inactive isomeride under the same conditions as in  $\alpha$  isomer, and found that pure dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate, thus formed, has the same melting point and specific rotatory power in its aqueous solution as in the active  $\gamma$  compound.

Hence, we may conclude that the primary cause in the autoracemisation of the optically active ammonium iodide in a chloroform solu-

tion would be ascribed to the decomposition of the compound into tertiary amine and alkyl iodide: subsequently the formation of the inactive ammonium iodide would take place, and the mechanism of the reaction may be represented as in the scheme already shown.

## *II. Cause of Autoracemisation of Optically Active Ammonium Compounds.*

As a matter of fact, the autoracemisation of optically active ammonium compounds takes place in a solvent of small dielectric constant, but there is found no precise relation to exist between the reaction velocity in a solvent and its dielectric constant and also between the reaction velocity of the substance and its solubility in a solvent.

Since the reaction actually takes place in a medium containing a halogen, it was supposed that the reaction may be caused by the catalytic action of halogen-acid generated by self decomposition of a solvent or of some other impurities which may come from the solvent during preservation.<sup>1</sup>

For this problem, the racemisation velocity of *α* dextro methyl allyl phenyl benzyl ammonium iodide in three kinds of chloroform solution, that is, in the purified chloroform kept for just one year in a dark cold place, in the freshly distilled chloroform and in the latter containing N/2000 HCl, was examined under the same conditions.

As seen in the results shown in the tables I, II, IV and VII, the impurity in chloroform exerts no remarkable influence upon the velocity of racemisation; in other words, the primary cause of the reaction should be ascribed to the action of the solvent itself but not to the catalytic action of halogen acid or some other impurities present in medium.

It was noticed by the author that optically active methyl *n*-propyl phenyl benzyl ammonium iodide in the allyl alcohol and acetonitrile solutions slowly lessened its rotatory power on standing, and moreover, though the rotatory power of the substance in ethyl alcohol solution did not change when left for three days in a tube carrying metallic mantel preventing the action of light, but in alcohol containing carbon tetrachloride, chlorobenzene, acetylen dichloride, amylene and cro-

<sup>1</sup> R. Walden: Ber. D. Chem. Ges., 31, 1422 (1898).

tonic acid, as seen in the experimental part the racemisation took place gradually.

From the experimental data, the author calculated approximately the time in which the half of the initial rotatory power of the active substance has been diminished, and from which the author have to compare the actions of solvents on the racemisation.

Solvents.	Time (in hours).
Chloroform $\text{Cl}_3\text{CH}$ .	3
Amylene $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$	3
Chlorobenzene $\text{Cl}\cdot\text{C}_6\text{H}_5$ .	48
Carbon tetrachloride $\text{CCl}_4$	49
Acetylen dichloride $\text{CHCl}=\text{CHCl}$	52
Acetonirile $\text{CH}_3\text{CN}$	53
Crotonic acid $\text{CH}_3\text{CH}=\text{CHCO}_2\text{H}$	58
Allyl alcohol $\text{CH}_2=\text{CHCH}_2\text{OH}$	119

These facts have induced the author to the notion that the decomposition of optically active substances would be caused by the common force which might exist in those solvents, and the author have to designate it as a residual affinity of solvents which may be due to the presence of a polyvalent element or unsaturated linking in molecule.

### *III. Thermal Effect in Optically Active Ammonium Compounds.*

By thermal analysis, the author has intended to study the chemical change of optically active compounds in the fused state.

When  $\alpha$  methyl allyl phenyl benzyl ammonium iodide in a fine powder was gradually heated in a tube over a sulphuric acid bath, the reading of thermometer which was inserted into the substance was observed to depress for a few degrees from  $120^\circ$  with the active substance, while with the racemic one from  $105^\circ$ .

It will be indicate that at these temperature the substances began to decompose.

Now the cooling curves for these substances have been plotted according to Tanmann's method which is applied to the investigation of alloys, and the results are shown in Fig. 2.

According to the author's investigation which is expected to be communicated in a near future we can imagine that a chemical change of a substance may occur in fusion being inferred from its cooling curve, and in the present case, it seems to the author that the substance have perfectly been decomposed into tertiary amine and alkyl iodide.

By chemically testing the fused mass, the presence of methyl allyl aniline and benzyl iodide was ascertained; consequently the author's assumption deduced from the cooling curve was realized.

Allowing the fused mass of a active substance to stand for a few days, methyl allyl phenyl benzyl ammonium iodide was obtained, which when purified by recrystallisation from alcohol, was confirmed to be inactive by polariscopic measurement.

Hence, the following conclusions may be drawn, when *a* dextro methyl allyl phenyl benzyl ammonium iodide is heated, it decomposes at about 120°, and in the fused state it splits up into methyl allyl aniline and benzyl iodide, which on standing recombine together forming inactive  $\gamma$  methyl allyl phenyl benzyl ammonium iodide as in the case with its chloroform solution.

#### EXPERIMENTAL PART.

Certain quantities of optically active ammonium compounds were dissolved in chloroform, and the solutions made up to 25 c.c. at constant temperature, and kept in a thermostat; each solution was taken in a 20 cm. glass tube of a polariscope which carries a metallic mantel to protect the action of light, and the observation of the angle of rotation conducted with sodium light.

In the experiments, the polarimeter tube was kept at a definite temperature, by letting the water of thermostat circulate through the mantel

The constant of the reaction-velocity was calculated by the formula of a monomolecular reaction.

**1.** 0.1232 gm.  $\gamma$  dextro methyl allyl phenyl benzyl ammonium iodide was dissolved in 25 c.c. chloroform which after purification had been kept for one year at a dark and cold place in the laboratory, and the rotatory power was observed at 25°, and the results are shown in the table I.



TABLE I.

$t$ (in minutes)	$\alpha$	$x$	$1-x$	$k = \frac{1}{t} \log \frac{1}{1-x}$
0	0.68°	—	—	—
25	0.64	0.0588	0.9412	0.0011
53	0.59	0.1324	0.8676	0.0012
86	0.50	0.2647	0.7353	0.0015
153	0.32	0.5294	0.4706	0.0022
223	0.26	0.6176	0.3824	0.0019
275	0.21	0.6912	0.3088	0.0018
343	0.11	0.8382	0.1618	0.0022
				Mean 0.0017

2. 0.1624 grm. of the same substance was dissolved in the same solvent as above, and its velocity of racemisation was determined at 30°.

TABLE II.

$t$ (in minutes)	$\alpha$	$x$	$1-x$	$k = \frac{1}{t} \log \frac{1}{1-x}$
0	0.77°	—	—	—
60	0.50	0.3506	0.6494	0.0031
125	0.20	0.7403	0.2597	0.0046
165	0.2	0.9740	0.0260	0.0035
				Mean 0.0038

From the Table I and II, the temperature coefficient of racemisation has been calculated as 4.5.

3. 0.1327 grm.  $\gamma$  lævo methyl allyl phenyl benzyl ammonium iodide was dissolved in the same chloroform and its velocity of the reaction was observed at 25°, and the results are shown in the table III.

TABLE III.

$t$ (in minutes)	$\alpha$	$x$	$1-x$	$k = \frac{1}{t} \log \frac{1}{1-x}$
0	0.51°	—	—	—
36	0.47	0.0784	0.9216	0.0010
86	0.37	0.2745	0.7255	0.0016
128	0.33	0.3530	0.6470	0.0015
221	0.29	0.4314	0.5686	0.0011

250	0.22	0.5295	0.4705	0.0014
346	0.14	0.7255	0.2745	0.0016
				Mean 0.0014

The velocity-constant at 25° is same with that of the antipode observed at the same temperature.

4. 0.1264 grm.  $\alpha$  dextro methyl allyl phenyl benzyl ammonium iodide was dissolved in the same chloroform above mentioned, and its velocity of racemisation was determined at 25°.

TABLE IV.

$t$ (in minutes)	$\alpha$	$x$	$1-x$	$k = \frac{1}{t} \log \frac{1}{1-x}$
0	0.39°	—	—	—
22	0.36	0.0769	0.9231	0.0015
52	0.30	0.2308	0.7692	0.0022
182	0.17	0.5641	0.4359	0.0019
				Mean 0.0019

5. 0.228 grm.  $\alpha$  dextro methyl allyl phenyl benzyl ammonium iodide was dissolved in the same chloroform, and its velocity of racemisation was observed at 30°. The results of the experiments are shown in the following table V.

TABLE V.

$t$ (in minutes)	$\alpha$	$x$	$1-x$	$k = \frac{1}{t} \log \frac{1}{1-x}$
0	0.90°	—	—	—
30	0.78	0.1333	0.8667	0.0021
82	0.57	0.3666	0.6334	0.0024
160	0.41	0.5444	0.4556	0.0021
225	0.25	0.7222	0.2778	0.0025
295	0.17	0.8111	0.1889	0.0025
				Mean 0.0023

As it was assumed that the impurities which may come from the solvents by decomposition or from some other unknown reactions

which is possible to take place during their preservation, might exert some influence upon racemisation, the following experiments were carried out by using the chloroform purified by distillation, after treating it with water and sulphuric acid successively.

6. 0.2245 gm. *a* dextro methyl allyl phenyl benzyl ammonium iodide was dissolved in 25 c.c. the purified chloroform, and its velocity of reaction was determined at 25°.

TABLE VI.

<i>t</i> (in minutes)	$\alpha$	$x$	$1-x$	$k = \frac{1}{t} \log \frac{1}{1-x}$
0	0.95°	—	—	—
95	0.75	0.2105	0.7895	0.0011
160	0.60	0.3684	0.6316	0.0012
215	0.46	0.5158	0.4842	0.0014
270	0.35	0.6316	0.3584	0.0015
343	0.21	0.7790	0.2210	0.0019
				Mean 0.0014

7. 0.227 gm. of the substance was dissolved in 25 c.c. of chloroform containing N/2000 hydrochloric acid, and its velocity of racemisation was determined at 25°.

TABLE VII.

<i>t</i> (in minutes)	$\alpha$	$x$	$1-x$	$k = \frac{1}{t} \log \frac{1}{1-x}$
0	0.91°	—	—	—
52	0.80	0.1209	0.8791	0.0011
143	0.63	0.3077	0.6923	0.0011
195	0.56	0.3846	0.6154	0.0011
260	0.37	0.5934	0.4066	0.0015
380	0.34	0.6264	0.3736	0.0011
				Mean 0.0012

8. 0.2062 gm. *lævo* methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in chloroform and the solution made up to 25 c.c. with chloroform and its velocity of reaction was observed at 25°.

The results as will be shown in the following table, is identical with that obtained by Wedekind.<sup>1</sup>

<sup>1</sup> *Loc. cit.*

TABLE VIII.

$t$ (in minutes)	$\alpha$	$x$	$1-x$	$k = \frac{1}{t} \log \frac{1}{1-x}$
0	1.44°	—	—	—
60	1.25	0.1320	0.8680	0.0010
117	1.00	0.3056	0.6944	0.0014
175	0.77	0.4653	0.5347	0.0016
225	0.58	0.5972	0.4028	0.0017
302	0.43	0.7012	0.2988	0.0017
380	0.24	0.8333	0.1667	0.0020

Mean 0.0016

9. 0.172 grm.  $\alpha$  dextro methyl allyl phenyl benzyl ammonium iodide was dissolved in 25 c.c. allyl alcohol from Kahlbaum, and the velocity of racemisation was observed at 25°.

TABLE IX.

$t$ (in hours)	0	81	119
$\alpha$	0.79°	0.44	0.39

10. 0.131 grm. lævo methyl  $n$ -propyl phenyl benzyl ammonium iodide was dissolved in 25 c.c. acetonitrile from Kahlbaum, and the racemisation-velocity was observed at 25°. The results will be shown in the following table.

TABLE X.

$t$ (in hours)	0	1	6	28	42
$\alpha$	0.70°	0.67	0.55	0.50	0.42

11. 0.1192 grm. lævo methyl  $n$ -propyl phenyl benzyl ammonium iodide was dissolved in alcohol containing 10 c.c. amylenes from Kahlbaum and the solution made up to 50 c.c. with alcohol at 25°, and the racemisation-velocity measured at 25°. When amylenes was added to alcoholic solution of the substance, the solution was found to colour instantly yellowish orange.

TABLE XI.

$t$ (in minutes)	0	85	170
$\alpha$	0.38°	0.28	0.20

**12.** 0.083 grm. lævo methyl *n*-propyl phenyl benzyl ammonium iodide and 5 grm.  $\alpha$ -crotonic acid from Kahlbaum were dissolved in 25 c.c. alcohol and the racemisation-velocity was examined with such solution. The results will be shown in the table XII.

<i>t</i> (in hours)	0	2	7	58
$\alpha$	0.58°	0.48	0.45	0.40

**13.** Lævo methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in alcohol containing 5 c.c. butyric acid and the solution made up to 25 c.c. with alcohol, and the angle of rotation of the solution was examined at 25°. It was observed that after 2 days the angle of the rotation of the solution was kept constant at  $\alpha_D = -0.25^\circ$

**14.** 0.0595 grm. lævo methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in alcohol, containing 5 c.c. carbon tetrachloride from Kahlbaum, and the solution made up to 25 c.c. with alcohol. The velocity of racemisation was observed at 25°.

TABLE XIV.

<i>t</i> (in hours)	0	4	9	32
$\alpha$	0.45°	0.42	0.35	0.30

**15.** 0.077 grm. lævo methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in alcohol, containing 5 c.c. acetylene dichloride and the solution made up to 25 c.c. with alcohol, and the racemisation-velocity of the solution was observed at 25°.

TABLE XV.

<i>t</i> (in hours)	0	9	27
$\alpha$	0.40°	0.35	0.29

**16.** Lævo methyl *n*-propyl phenyl benzyl ammonium iodide was dissolved in a mixture of 40 c.c. alcohol and 10 c.c. chlorobenzene from Kahlbaum, and the racemisation-velocity of the solution was observed.

TABLE XVI.

<i>t</i> (in hours)	0	51	123
$\alpha$	0.22°	0.20	0.5

*17. Chemical Change of  $\alpha$  Dextro Methyl Allyl Phenyl Benzyl Ammonium Iodide in the Chloroform Solution.*

**A.** Pure  $\alpha$  methyl allyl phenyl benzyl ammonium iodide was resolved into its optically active components by means of silver dextro-camphorsulphonate.

$\alpha$  Dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate recrystallized from acetone 5 times, was found to melt at  $162^\circ$  and its rotatory power in an aqueous solution was determined.

A solution of 0.2159 grm. substance made up to 25 c.c. with water at  $25^\circ$ , gave  $\alpha_D^{25} = +1.0^\circ$  in a 20 cm. tube; whence  $[\alpha]_D^{25} = +46.54^\circ$ .

A solution of 0.4535 grm. substance made up to 25 c.c. with water at  $25^\circ$ , gave  $\alpha_D^{25} = +1.67^\circ$  in a 20 cm. tube; whence  $[\alpha]_D^{25} = +46.03^\circ$ .

**B.** 7 grm. pure  $\alpha$  ammonium iodide above mentioned was dissolved in 150 c.cm. chloroform from Kahlbaum, and the solution was left to stand for 3 days in the laboratory, during which time its colour changed yellowish orange.

After distilling off the solvent, there was left a dark brownish orange syrupy residue from which pure methyl allyl phenyl benzyl ammonium iodide was isolated, and its yield was found to be 3.5 grm. The melting point of the substance was noticed to be  $127-128^\circ$ .

3.5 grm. the iodide and 3.5 grm. silver camphorsulphonate were mixed in acetone-acetic ester, and the mixture treated as usual.

Pure dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate crystallized from acetone 4 times, possesses the melting point  $165-166^\circ$ , and the same physical and chemical properties as those of the active  $\alpha$  compound.

A solution of 0.2792 grm. substance made up to 25 c.c. with water at  $25^\circ$ , gave  $\alpha_D^{25} = +1.14^\circ$  in a 20 cm. tube; whence  $[\alpha]_D^{25} = +51.04^\circ$ .

**C.** 20 grm. pure  $\alpha$  methyl allyl phenyl benzyl ammonium iodide was heated, dissolved in 300 c.c. chloroform at  $62^\circ$  for one day. After such a treatment, the solvent was distilled off and a part of the residue treated with ether to dissolve the decomposition products contained in it. From the ethereal solution, methyl allyl aniline and benzyl iodide were obtained, and the latter was identified by converting into benzaldehyde by oxidation with copper nitrate.

Methyl allyl aniline was analysed by changing it into ferrocyanide, and the result was as follows :

0.115 grm. amine ferrocyanide gave 0.0205 grm.  $\text{Fe}_2\text{O}_3$  on ignition.

	Calc. for $\text{C}_{26}\text{H}_{39}\text{N}_8\text{Fe}$ .	Found.
Iron	10.96	12.54

Another part of the residue was allowed to stand, solidifying in a crystalline mass from which 6 grm. pure methyl allyl phenyl benzyl ammonium iodide were obtained and its melting point was found to be  $125-126^\circ$ .

6 grm. pure iodide was mesotomized with 6 grm. silver dextro camphorsulphonate in the acetone-ethyl acetate solution. The reaction product was mercerized with acetone 3 times and once with ethyl acetate.  $\alpha$  Dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate, thus obtained, consisted of fine needle-shaped crystals melting at  $162-163^\circ$  and its yield was found to be 0.2 grm.

The rotatory power of the aqueous solution was determined and the result will be mentioned in the following statements :

A solution of 0.14 grm. substance made up to 25 c.c. with water at  $25^\circ$ , gave  $\alpha_D^{25} = +0.66^\circ$  in a 20 cm. tube, whence  $[\alpha]_D^{25} = +58.93^\circ$ .

Dextro methyl allyl phenyl benzyl ammonium iodide obtained from the above camphorsulphonate, crystallizes from ethyl alcohol in fine white needles which melt at  $133-134^\circ$ .

A solution of 0.0513 grm. substance made up to 25 c.c. with alcohol at  $25^\circ$ , gave  $\alpha_D^{25} = +0.28^\circ$  in a 20 cm. tube ; whence  $[\alpha]_D^{25} = +68.23^\circ$ .

**D.** 10 grm. crude  $\alpha$  dextro methyl allyl phenyl benzyl ammonium iodide was kept to boil in the chloroform solution at  $62^\circ$  for 3 days on a water bath. Letting the syrupy residue for 5 days stand, it solidified to a crystalline mass, from which 3 grm. methyl allyl phenyl benzyl ammonium iodide was isolated.

3 grm. of the iodide was treated with 3 grm. silver camphorsulphonate in acetone-ethyl acetate solution as usual. The reaction product was made to recrystallize from acetone 4 times and ethyl acetate 2 times successively, and dextro methyl allyl phenyl benzyl ammonium dextro-camphorsulphonate melting at  $162-163^\circ$  was obtained in fine colourless needles, and its yield was found to be about 0.18 grm.

A solution of 0.156 grm. substance made up to 25 c.c. with water at 25°, gave  $\alpha_D^{25} = +0.74^\circ$  in a 20 cm. tube; whence  $[\alpha]_D^{25} = +58.75^\circ$ .

Dextro methyl allyl phenyl benzyl ammonium iodide obtained by adding potassium iodide to the aqueous solution of the camphorsulphonate above mentioned, was found to melt at 133–134°.

A solution of 0.061 grm. substance made up to 25 c.c. with alcohol at 25°, gave  $\alpha_D^{25} = +0.31^\circ$  in a 20 cm. tube; whence  $[\alpha]_D^{25} = +63.52^\circ$ .

**18.** *Chemical Change of  $\gamma$  Methyl Allyl Phenyl Benzyl Ammonium Iodide in the Chloroform Solution.*

$\gamma$  Methyl allyl phenyl benzyl ammonium iodide was heated in chloroform solution at 62° for one day, and the solution treated in the same manner as in  $\alpha$  compound.

5 grm. methyl allyl phenyl benzyl ammonium iodide, thus obtained was treated with 5 grm. silver dextro camphorsulphonate in acetone-ethyl acetate solution.

The reaction product was made to recrystallize from acetone 2 times and ethyl acetate once.

Dextro methyl allyl phenyl benzyl ammonium dextrocamphorsulphonate consists of fine colourless needles melting at 161–162°, and its yield was found to be 0.18 grm.

A solution 0.1784 grm. substance made up to 25 c.c. with water at 25°, gave  $\alpha_D^{25} = +0.80^\circ$  in a 20 cm. tube; whence  $[\alpha]_D^{25} = +56.06^\circ$ .

Dextro methyl allyl phenyl benzyl ammonium iodide obtained from camphorsulphonate above mentioned, crystallizes from alcohol in white needles; its rotatory power was determined in a alcoholic solution.

A solution of 0.0875 grm. substance made up to 25 c.c. with alcohol at 25°, gave  $\alpha_D^{25} = +0.44^\circ$  in a 20 cm. tube; whence  $[\alpha]_D^{25} = +65.71^\circ$ .

**19.** *Experiment on the Fused  $\alpha$  Methyl Allyl Phenyl Benzyl Ammonium Iodide.*

**A.** When 0.7 grm. pure  $\alpha$  dextro methyl allyl phenyl benzyl ammonium iodide (its specific rotatory power in alcoholic solution is  $[\alpha]_D^{25} = +52.38^\circ$ ) made in a fine powder, was gradually heated in a Jena-glass tube of 8 mm in diameter on a double walled sulphuric acid bath, it changed yellow at 115°, and at 124° the height of the



thermometer inserted into the substance ceased to rise for 20 seconds, and then it changed to an orange red fluid perfectly at 144°.

The cooling velocity of the fused mass was observed, and a curve was plotted with the times and temperatures. The result will be shown in Fig. 2 (denoted in a dotted line). Allowing it to stand for 2 days it solidified to a crystalline mass, from which methyl allyl phenyl benzyl ammonium iodide was isolated.

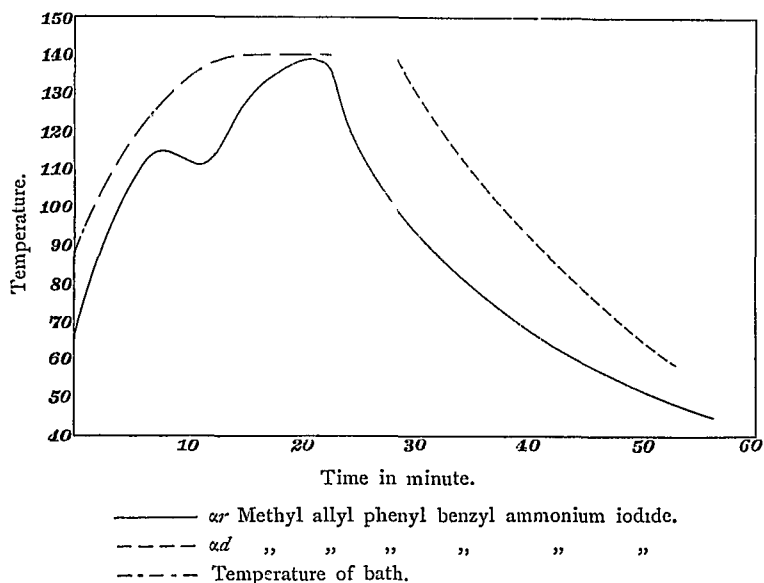


Fig. 2.

The substance recrystallized from alcohol, melted at 125–126°, its alcoholic solution having been observed to be inactive.

**B.** 3 grm pure methyl allyl phenyl benzyl ammonium iodide, was heated under the same condition as for the active compound, but it was observed to decompose at about 114.5°

The thermal change of the substance and the rate of cooling of the fused mass, was plotted as shown in Fig. 2 (in a thick line).

By treating the fused mass with ether, it was almost entirely dissolved leaving a trace of reddish brown mass. The ethereal solution was treated with dilute hydrochloric acid, and from the upper layer of the solution, benzyl iodide was isolated, which was converted into benzaldehyde by oxidation with copper nitrate and the aldehyde was identified by its phenylhydrazone (mp. 152°) and also by its odour.

The acidic lower layer of the solution was neutralized with caustic soda and extracted with ether. Evaporating the ether, there remained an yellow oil which was confirmed to be methyl allyl aniline by analysis of its ferrocyanide and by the melting point of the picrate.

0.10 grm. the ferrocyanide gave 0.0158 grm.  $\text{Fe}_2\text{O}_3$ , on ignition.

	Calc. for $\text{C}_{20}\text{H}_{39}\text{N}_3\text{Fe}$ .	Found.
Iron	10.96	11.08

Allowing the fused mass of the iodide to stand for 3 days, it solidified to a crystalline mass from which pure methyl allyl phenyl benzyl ammonium iodide was isolated. The substance melts at  $123-124^\circ$ , and by analysis gave the following results:

0.104 grm. substance gave 0.067 grm. AgI.

	Calc. for $\text{C}_{16}\text{H}_{20}\text{NI}$	Found.
Iodine,	34.79	34.82

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